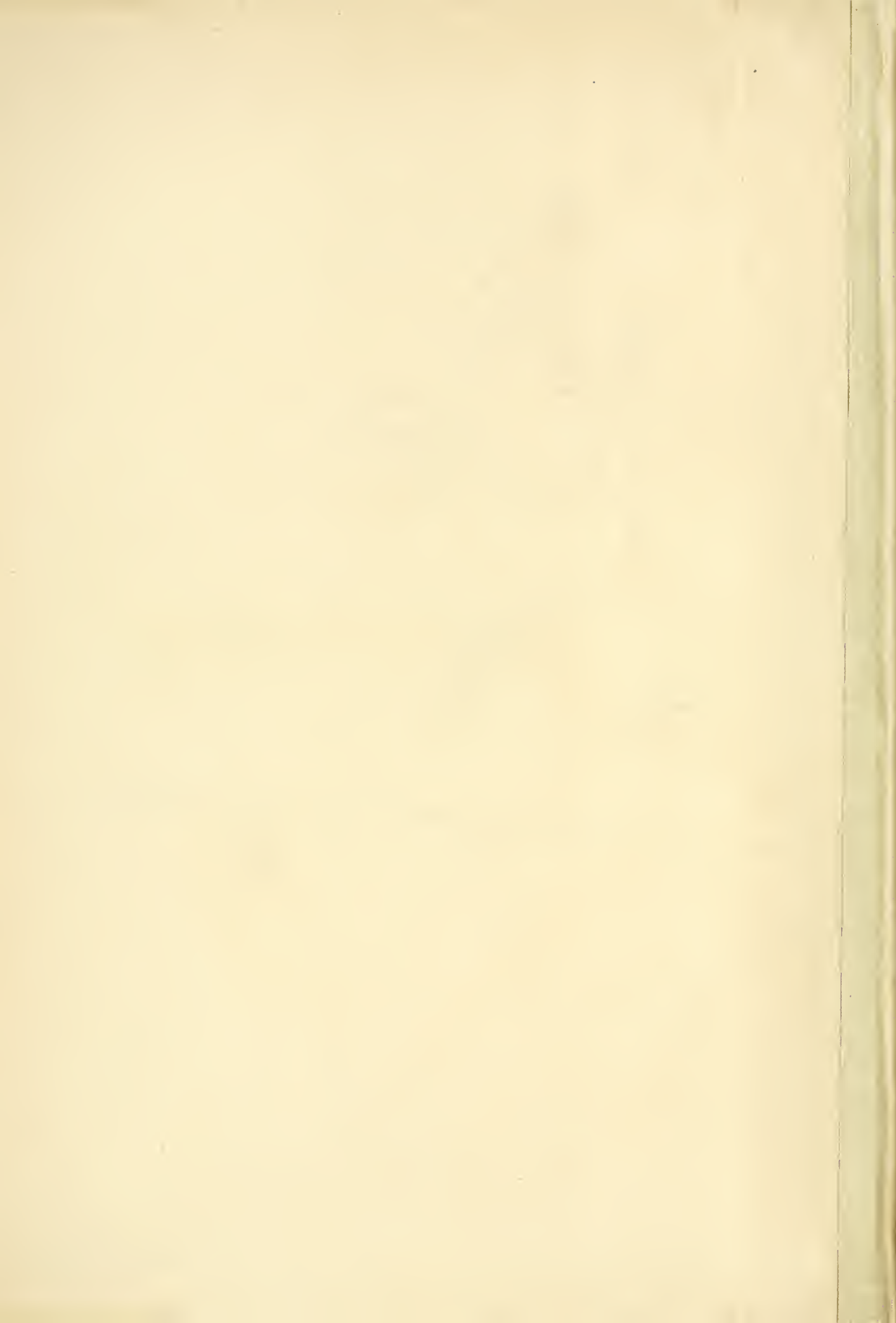
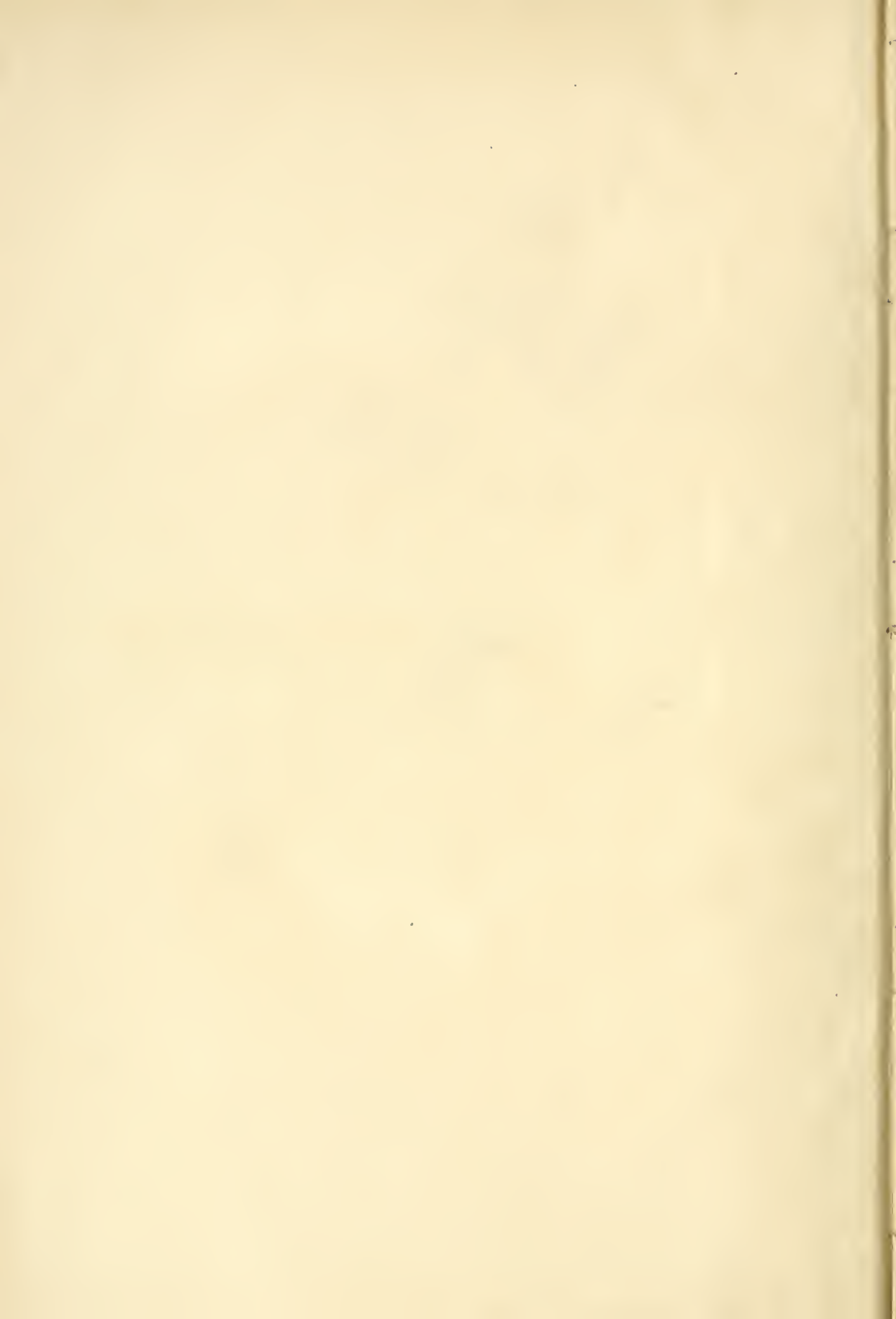


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THE CHEMICAL NEWS, JULY 20, 1906.

THE

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THE CHEMICAL NEWS.

VOLUME XCIII.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2406.—JANUARY 5, 1906.

THE PHYSICAL AND CHEMICAL PROPERTIES OF IRON CARBONYL.*

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S.,
Jacksonian Professor in the University of Cambridge,
and

HUMPHREY OWEN JONES, M.A., D.Sc., Fellow of Clare
College, and Jacksonian Demonstrator in the University of Cambridge.

This paper contains an account, as promised, of a study of the physical and chemical properties of iron carbonyl, similar to that already communicated to the Society, on the properties of the analogous compound of nickel, to which this forms the sequel (*Proc. Roy. Soc.*, 1903, vol. lxxi., p. 427).

The combination of iron and carbon monoxide was discovered by Drs. Mond and Quincke in 1891 (*Trans. Chem. Soc.*, 1891, vol. lix., p. 604), and the resulting compound called iron pentacarbonyl was isolated (as a coloured liquid), and examined by Drs. Mond and Langer in the course of the same year (*Trans. Chem. Soc.*, vol. lix., p. 1090).

Our knowledge of this remarkable substance is derived entirely from the observations of the last-named investigators, and a few isolated observations of others—thus the late Dr. Gladstone determined its refractive indices and Dr. Perkin the magnetic rotation. The molecular refractive power and magnetic rotation are abnormally high, and the compound is diamagnetic; such remarkable properties naturally aroused considerable interest, but the lack of any further work on the compound is doubtless due to the great difficulty experienced in preparing quantities of the compound large enough to work with.

The peculiarities exhibited by this compound call for further attention, and we have examined the formation of the compound and its properties, both physical and chemical; the investigation has been carried out on the same lines as that on nickel carbonyl (*loc. cit.*, and *Trans. Chem. Soc.*, 1904, vol. lxxxv., pp. 203, 213), and attention has been directed more particularly to the differences between the iron and nickel carbonyls, such as the difference in formula, colour, stability, and, more especially, to the action of light on iron carbonyl.

We are indebted to Dr. Mond for two specimens of iron carbonyl with which the investigation was begun; latterly we have been able to prepare and use much larger quantities of the compound, and further work is still in progress. The preparation of iron carbonyl in quantity is a long and tedious process; the yield obtained depends on a number of circumstances; the best conditions for the preparation of the compound are being investigated, and it is hoped that the observations made on this subject will form the subject of another communication.

Liquid iron carbonyl is described as a yellow liquid, with the formula $\text{Fe}(\text{CO})_5$, boiling at 102.8°C . It is remarkable that nickel carbonyl, the compound of a metal whose salts are highly coloured, is colourless, while iron carbonyl is coloured, and the salts of iron have usually only a feeble colour. Also the difference in composition, coupled with the higher boiling-point of the iron compound, caused by the introduction of more carbon monoxide, is a striking phenomenon. We consider it important to determine whether careful purification and drying of the compound would remove the colour, and to procure further analytical evidence bearing on its formula.

To purify the substance it was placed with some suitable drying agent (copper sulphate, barium oxide, zinc chloride, and pure phosphorous pentoxide were all found suitable) in one limb of a carefully-dried glass tube bent into the form of a V-tube; the other limb was empty. The tube was then exhausted by means of a side tube, filled several times with carbon monoxide, hydrogen, or nitrogen, exhausted again, and then the side tube was sealed off. After standing in the dark for some time the iron carbonyl was distilled into the empty limb by placing this in a freezing mixture and the other limb in a beaker of water at about 50°C . The liquid was still of a pale yellow colour, even after standing several days over phosphorous pentoxide and distilling by feeble gas-light.

Another form of experiment showed conclusively that the colour is a definite property, and is not due to impurities. A tube bent into the form of an M was used, the liquid was allowed to stand in one limb for several days over anhydrous copper sulphate, distilled over into the bend, where it was allowed to stand for a week over pure phosphorous pentoxide, and then finally distilled into the empty limb of the tube. The operations were carried out in the dark, and the liquid still possessed its yellow colour. Consequently, it is concluded that the pure compound has a yellow colour. We have therefore not been able to confirm the opinion expressed by Armstrong that the pure compound would be colourless (*Proc. Chem. Soc.*, 1893, p. 58).

For analysis the compound was purified as described above, and rapidly transferred to weighed glass bulbs in a vacuum desiccator, the bulbs sealed and weighed. The transference must be effected very rapidly, as the compound is exceedingly sensitive to air and moisture; a reddish precipitate is produced on standing if the liquid has been exposed even for a very short time to moist air.

The percentage of carbon monoxide was determined by combustion. It was found necessary, in order to get constant results, to pass a current of oxygen through the tube for a long time, while heated to a bright red heat, in order to completely oxidise the carbon which was deposited with the iron.

* A Paper read before the Royal Society, November 16, 1905.

1. 0.2680 grm. of the liquid gave 0.3000 grm. of carbon dioxide.
2. 0.4336 grm. of the liquid gave 0.4825 grm. of carbon dioxide.

The estimation of the iron offered greater difficulties. Mond and Langer (*loc. cit.*) decomposed the compound by heating to 100° C. with chlorine or bromine water in a sealed tube, and then weighing the iron as ferric oxide.

This method always gave slightly high results, and accuracy is limited because small quantities only can be used on account of the great pressure developed.

3. 0.3417 grm. gave 0.1429 grm. of ferric oxide.

A bulb containing a weighed quantity of the liquid was broken under a chloroform solution of bromine, the gas evolved was passed through more of the same solution in a U-tube. When the reaction had ceased the solutions were evaporated to dryness, and the iron precipitated and weighed as ferric oxide.

4. 0.7820 grm. gave 0.3209 grm. ferric oxide.

The best method of decomposing the compound was found to be treatment with alcoholic potash solution in a sealed tube at 100° C. When a bulb containing pure iron carbonyl was broken in alcoholic potash solution, beautiful colourless tabular crystals having a pearly lustre were at once produced; at the surface of the liquid these were at once oxidised by the air with the formation of a reddish brown precipitate.

The mixture contained in a sealed tube was heated to 100° C. for a short time, the tube cooled, opened (no pressure is produced by this decomposition), the contents washed out, and evaporated to dryness. The residue was treated with nitric acid, again evaporated down, and the iron precipitated by hot caustic potash to separate it from aluminium which was dissolved out of the glass.

5. 0.9465 grm. gave 0.3886 grm. ferric oxide,

Several other methods of analysis were also tried, such as decomposing the carbonyl by heat, weighing the iron, and measuring the carbon monoxide. A small bulb containing a weighed quantity of the purified iron carbonyl was placed inside a strong glass bulb, a glass tap was then sealed on to this, the bulb exhausted with a Töpler pump, the small bulb was broken, and the carbonyl decomposed by heating to about 180° to 200° C. until no deposit of iron could be produced by heating a clear portion of the large bulb with a blowpipe flame.

The carbon monoxide was then removed, by means of a Töpler pump, and measured; the bulb with the deposited iron was weighed, the iron dissolved off, and the bulb weighed again after drying. In this process it was found that the glass was often attacked where the iron had been deposited, and the high values obtained for the iron are doubtless to be attributed to this cause and to the presence of carbon in the iron (see later). The following example illustrates the kind of result obtained by this method:—

6. 0.4626 grm. gave 287 c.c. of carbon monoxide at 19° C. and 757 m.m., and left 0.1371 grm. of iron.

Found—	Fe.	CO.	CO by volume for 1 grm.
1	—	71.2	—
2	—	70.9	—
3	29.2	—	—
4	28.7	—	—
5	28.7	—	—
6	29.6	—	564.2 c.c. at 0° C. of 760 m.m.

Calculated for—

Fe(CO) ₅	28.57	71.43	571.4 c.c.
Fe(CO) ₄	33.33	66.66	530.9 c.c.

The compound is therefore Fe(CO)₅.

Attempts were made to determine the ratio Fe:CO in the compound by passing nitrogen through a weighed or unweighed quantity of pure iron carbonyl, and then

through a glass tube bent twice on itself, and heated in a bath so that the vapour was heated for some time, and decomposed into iron and carbon monoxide; the iron was deposited in the tube, and then weighed, the carbon monoxide was passed over hot copper oxide and weighed as carbon dioxide in a potash tube. It had been found previously that this process gave good results in the case of nickel carbonyl.

With iron carbonyl, however, consistent results could never be obtained. In the first place the compound is much more difficult to decompose completely than nickel carbonyl, and it was found that, in order to ensure complete decomposition, it was necessary, when keeping the bath at 180° to 200° C., to heat a small portion of the tube nearer the copper oxide tube nearly to redness. Even then it was always found that the sum of the weights of the iron and carbon monoxide was always less than that of the iron carbonyl taken. This was traced to the fact that the iron deposited was always contaminated with carbon, which was given off as hydrocarbons when the iron was dissolved in acids; also the weight of ferric oxide obtained from the iron was always less than it should have been. The ratio CO:Fe was usually about 4.5 to 4.8; this is readily accounted for by a small percentage of carbon in the iron. The presence of carbon in the iron would also tend to raise the percentage of iron as estimated by Method 6.

Further evidence in support of the formula Fe(CO)₅ was afforded by experiments on the decomposition of the vapour enclosed in a space at a given pressure and measuring the pressure of the carbon monoxide produced; this was approximately five times the original pressure of the vapour. These experiments will be referred to later.

Molecular Weight.—Numerous vapour-density determinations have been made, and will be described in another part of this paper. When no dissociation occurs the vapour density varied between 98 and 100, so that the molecular weight corresponds to the formula Fe(CO)₅ with a molecular weight of 198.

Two determinations of the molecular weight in benzene were made by the cryoscopic method; a weighed quantity of liquid in a bulb was broken under the benzene. Owing to the very great sensitiveness of the compound air and moisture, the solution always began to turn turbid before the end of the experiment, even when the greatest care was taken to exclude moisture and the air in the apparatus had been replaced as completely as possible by nitrogen or carbon monoxide.

- 0.2956 grm. in 14.28 grms. benzene gave a depression of 0.524° C. Hence the molecular weight is 197.
- 0.3900 grm. in 14.20 grms. benzene gave a depression of 0.705° C. Hence the molecular weight is 194.

Specific Gravity of the Liquid.—Mond and Langer (*loc. cit.*) gave the density of liquid iron carbonyl as 1.4664 at 18° C. compared to water at the same temperatures, or 1.4688 compared to water at 4° C. Gladstone (*Phil. Mag.*, 1893, [5], vol. xxxv., p. 204) gave the density at 13.4° C. as 1.474, at 15.5° C. as 1.470, and at 22° C. as 1.460.

The specific gravity was determined with the aid of a small glass pycnometer (volume 2.2 c.c.) at temperatures from 0° C. to 80° C. Great care was exercised to exclude moisture, and the experiments were carried out in a dim light; a very small amount of decomposition, indicated by the formation of minute bubbles of gas, always took place, which was more marked at the higher temperatures, and was doubtless caused by traces of moisture and air, so that the numbers obtained can only be regarded as approximate for the two highest temperatures. The specific gravity is in each case referred to water at 4° C.

Temperature.	Specific gravity.
0.0° C.	1.494
16.5° C.	1.468
40.0° C.	1.421
61.5° C.	1.382
80.0° C.	1.351

These specific gravity determinations were made with a specimen of the carbonyl kindly supplied by Dr. Mond. When a much larger quantity was available this was purified, and further determinations were made with a much larger pycnometer (volume 7.1100 c.c.), using the same precautions (in this case there were no signs of any decomposition).

Temperature.	Specific gravity.
0° C.	1.4937
21° C.	1.4565
40° C.	1.4330
60° C.	1.3825

These results agree fairly well with those given above, but are naturally most trustworthy on account of the larger quantity of material used.

The coefficient of expansion for 0° C. to 21° C. is 0.00121, for 21° C. to 40° C. is 0.00128, and for 40° C. to 60° C. is 0.00142. The mean coefficient of expansion is therefore about 0.00138.

By extrapolation on the curve the specific gravity at the boiling-point, 102.5° C., is 1.310. The molecular volume is therefore 149.6. At the melting-point, -20° C., the specific gravity is 1.53 and the volume of the molecule is then about 128.

The values of the specific gravity of the liquid at 0° C. and 60° C., taken with the critical temperature (288° C., for which see *prox.*), give the following Waterston formula for the relation between the volume v and the temperature t° C. :—

$$v = 1.974 \cdot 0.5307 \log (288 - t^{\circ}).$$

Refractive Indices.—Gladstone (*loc. cit.*) determined the refractive indices of the carbonyl for several of the lines of the spectrum, and found that, as in the case of nickel carbonyl, the compound had a very large molecular refractive power and an enormous dispersive power. It was therefore unnecessary to investigate this property minutely, and two determinations only were made for sodium and thallium light with an Abbé refractometer by Mr. A. Hutchinson, of the Mineralogical Department.

μ for Na light	1.519
μ „ „ „	1.528 at 22° C.

These values agree very closely with those found by Gladstone—1.5180 and 1.5289.

Melting-point.—The pale yellow liquid crystallises when cooled to a pale yellow solid which melts at -19.5° C. to -20° C. At the temperature of liquid air the solid entirely loses its colour, which it gradually recovers on warming up again.

Vapour Pressure and Boiling-point.—The vapour pressure was determined by the statical method as in the case of nickel carbonyl.

A wide barometer tube, drawn off to a fine capillary at one end, was carefully cleaned and placed upright in a vessel of pure dry mercury, in a room lighted by a feeble gas-jet. A small tube containing iron carbonyl was now introduced, the whole exhausted thoroughly by means of a Fleuss pump, and sealed off at the end. The pressure was then read off by means of a kathetometer, while the tube was surrounded by a bath at various temperatures. Observations taken after cooling and allowing the tube to stand showed that no appreciable amount of decomposition took place under the conditions of the experiment. The results are appended below :—

Temperature.	Pressure.
-7° C.	14.0 m.m.
0° C.	16.0 „
16.1° C.	25.9 „
18.4° C.	28.2 „
35.0° C.	52.0 „
57.0° C.	133.0 „
78.0° C.	311.2 „

Next day at 18.9° C. the pressure was 29.4 m.m.

The boiling-point given by Mond and Langer is 102.8° C. at 749 m.m. Several determinations of the boiling-point were made, all of which gave a result slightly lower than this. Thus, it was found that the liquid boiled at 101.8° C. at 736 m.m., at 102.0° C. at 744 m.m., and at 102.7° C. at 764 m.m. The values for 0° C. and 102.7° C. give the following Rankine formula for the relation between the vapour pressure p in m.m. of mercury and the absolute temperature T :— $\log p = 7.349 - 1681/T$. This fits in very well with the results for the intermediate temperatures.

Critical Temperature.—It was found by trial experiments that the liquid could be heated in a glass tube under pressure to temperatures considerably above its boiling-point without undergoing noticeable decomposition. Its critical temperature was therefore determined by placing some liquid in small thick-walled capillary tubes, exhausting, sealing-off, and then heating the tubes in an air- or paraffin-bath until the meniscus disappeared. The tubes were about one-third to one-half full of liquid, and though no deposit of iron was produced, yet the tubes burst after heating several times to the critical point. In several determinations it was found that the meniscus disappeared between 285° C. and 288° C.

The formula $T = 0.66 T_c$, where T_c is the absolute boiling-point and T the absolute critical temperature, is usually applicable to liquids which are not associated in the liquid or gaseous state near the boiling-point, and was found to be applicable to nickel carbonyl; it should therefore be applicable here. Taking the boiling-point as 102.5° C., the critical temperature should be 289.2° C., a value agreeing very closely with the number found experimentally.

The critical density of iron carbonyl is calculated to be 0.49, the value for nickel carbonyl is 0.46. The critical pressure calculated from the Rankine formula for the vapour pressure is 29.6 atmospheres.

The number obtained by dividing the absolute critical temperature by the critical pressure, which is proportional to the volume of the molecule, Van der Waal's constant b , is 18.9, the corresponding value for nickel carbonyl is 15.5, and the value for carbon monoxide is 3.7. Hence the volume of the molecule of iron carbonyl is 5.1 times larger than that of carbon monoxide, while 4.2 represents the ratio for the nickel carbonyl.

The latent heat of iron carbonyl is 39.45 calories per grm., and the Trouton constant, molecular latent heat divided by absolute boiling-point, is 20.6, a value identical with that for nickel carbonyl.

The molecular volume of iron carbonyl at its boiling-point is 150, so that taking 7.0 as the volume of the iron atom, we get 28.6 as the volume of each carbon monoxide molecule, a number smaller than that found for nickel carbonyl, *i.e.*, 32.2. Liquid carbon monoxide at its boiling-point has a molecular volume of 35, so that a greater contraction would take place in the formation of liquid iron carbonyl from liquid carbon monoxide and iron, if that were possible, than in the formation of nickel carbonyl under similar conditions.

The similarity between many of the constants of nickel and iron carbonyls is very striking, in spite of the fact that the substances differ so widely in their boiling-points and stability.

(To be continued).

“Annuaire du Bureau des Longitudes.”—The house of Gauthier-Villars, of Paris, has just published the 1906 edition of the above useful annual. In this compact volume are to be found, as usual, a fund of information equally interesting to the engineer, the physicist, and the chemist. We may specially mention a well-illustrated article by G. Bigourdan on Eclipses of the Sun, with instructions as to observations which can be made during an eclipse. The book contains nearly 900 pages, 16mo., and has that rarity in a French book, a good alphabetical index.

THE CANYON DIABLO METEORITE.

Coon Mountain and its Crater.—Dr. Dixon announced that Mr. Daniel Moreau Barringer and Mr. Benjamin Chew Tilghman, members of the Academy, had notified him of their discovery that the crater of Coon Mountain or Coon Butte, in Northern Arizona, twelve miles south-east of Cañon Diablo Station on the Atchison, Topeka, and Santa Fé Railway, is an impact crater and not a crater produced by a steam explosion, as has been supposed since the examination made of it by members of the United States Geological Survey. They have proved, by a large amount of development work, according to their statements, that the large crater and elevation known as Coon Mountain is the result of a collision with the earth of a very large meteorite or possibly a small asteroid, fragments of which are well known to the scientific world by the name of the Cañon Diablo siderites. Their development work, consisting of cuts, shafts, and bore-holes, has established the following facts:—

1. That the formation of the crater and the deposition of the meteoric material were simultaneous.
2. That meteoric material has been found five hundred feet below the surface of the centre of the crater.
3. That sandstone supposed to be in place exists less than one thousand feet below the surface of the centre of the crater.

Mr. Barringer and Mr. Tilghman have presented to the Academy for publication two comprehensive papers in which they set forth in full their reasons for the above statements.—*Proceedings of the Academy of Natural Sciences of Philadelphia*, December 5, 1905.

NEW RESEARCHES ON THE ATOMIC WEIGHT OF NITROGEN.*

By PHILIPPE A. GUYE.

(Continued from vol. xcii., p. 287).

III.

HAVING demonstrated our second thesis, we have to express the results relative to the atomic weight of nitrogen to which the different methods just discussed lead. We will first recall the figures at which the different authors have successively arrived.

Leduc (molecular volumes, 1897)	14'005
Berthelot (density limits, 1898)—	
Starting from N ₂	14'007
" " N ₂ O	14'000
Guye and Friederich (density limits, 1900)—	
Starting from N ₂	14'005
Lord Rayleigh (density limits, 1905)—	
Starting from N ₂	14'008
" " N ₂ O	13'998
Guye (reduction of critical elements, 1905)—	
Starting from N ₂	14'007
" " N ₂ O	14'006
" " NO	14'009
Gray (density limit, 1905)—Starting from NO ..	14'006

The mean of the determinations of 1905, which are the most accurate—excluding the evidently too low value furnished by the density limit of N₂O—is $N = 14'007$.

The variations between these different determinations are due, in part at least, to the different selections which were made of the different density determinations, in part equally to the fact that one is not always placed under conditions reducing to a minimum the correction for the density of the gas which results from the experiment.

These conditions are best realised as follows:—

When the densities, L and L' , of any two gases are compared, the molecular weight, M , found will bear to the known molecular weight, M' , a relation of the form—

$$M = M' \frac{L}{L'} \frac{(1 + \lambda)}{1 + \lambda'} = M' \frac{L}{L'} (1 + \epsilon);$$

in which $(1 + \lambda)$ and $(1 + \lambda')$ represent the correction factors calculated by one or other of the four methods that we have just described. For brevity, we write—

$$\frac{1 + \lambda}{1 + \lambda'} = 1 + \epsilon.$$

If, instead of comparing all gases to one taken as standard (oxygen), the comparisons are limited to gases taken in two's, so that for each pair of gases the critical constants T_c and p_c are near, or at least of the same order of magnitude, it is evident that the factor $(1 + \epsilon)$ will be very near unity. It is therefore under these conditions that the greatest degree of accuracy is obtained with certainty, and it is of all the greater interest to endeavour to realise them, that the theory of corresponding states, upon which all the physico-chemical methods depend, is not absolutely rigidly expressed as a physical law; this repeats that the physico-chemical calculation of the molecular weight of a gas represents as yet an approximation. It is therefore of great interest to work under conditions giving the greatest degree of accuracy. One is the more forced to consider as exact the corrections deduced from this theory in proportion as the latter are themselves slight.

This method of procedure presents another advantage: it places in evidence the numerical value of the correction factor $(1 + \epsilon)$ obtained by each of the physico-chemical methods, and also estimates the degree of concordance with which it is determined.

The following are the results which are thus obtained with the nitrous gases:—

Corrected Ratio of the Densities of Nitrogen and Oxygen.

—The ratio of the densities of these two gases resulting directly from experimental data at 0° and 1 atmosphere is—

16 $L'/L = 14'003$ (Rayleigh), 16 $L'/L = 14'001$ (Leduc).

A mean value may therefore be adopted,—

$$16 L'/L = 14'002.$$

The correction factor determined by physico-chemical methods has the following values, in connection with which are inscribed the atomic weights of nitrogen obtained by correcting the rough value 14'002.

TABLE IX.

Methods.	Correction factor.	N.
1. Density limits at 0°:—		
Berthelot	1'00038	14'008
Rayleigh	1'00038	14'008
2. Reduction to 0° of the critical elements:—Guye	1'00044	14'008
3. Corresponding densities:—		
N ₂ , 37°/503; O ₂ , 100°/760 (Guye)	1'00085	14'014
Corresponding temperature, Avogadro (Guye)	1'00061	14'011
Corresponding molecular vol. at 0° (Leduc)	1'0004	14'008
4. Densities at 1067° (Jaquero and Perrot)	1'00043	14'008
Mean	1'00050 × 14'002	14'009

Corrected Ratio of the Densities of the Gases N₂ and CO.

—The direct ratio of these densities, calculated from experimental data, putting CO = 28'002, is—

28'002 $L/L' = 28'008$ (Rayleigh),

28'002 $L'/L = 28'006$ (Leduc).

* From the *Bulletin de la Société Chimique de Paris*, 1905

From the agreement of these results, a single mean value may be adopted—

$$28.002 \text{ L/L} = 28.007.$$

The values of the correction factor, determined by different methods, are placed in the following table, together with (1) the resulting molecular weight M of nitrogen; (2) the corresponding atomic weight N:—

TABLE X.

Methods.	Correction factor.	M.	N.
Density limits (Berthelot) . . .	1.00008	28.009	14.005
" (Rayleigh) . . .	1.00025	28.014	14.007
Reduced to 0° of the critical element (Guye) . . .	1.00017	28.012	14.006
Corresponding density: N ₂ , -11° 719; CO, 0°/760 (Guye)	1.00014	28.011	14.006
Corresponding temperature, Avogadro (Guye) . . .	1.00014	28.011	14.006
Corresponding molecular volume, 0° (Leduc) . . .	1.00001	28.010	14.005
Mean . . .	1.00015	28.011	14.006

Corrected Ratio of the Densities of the Gases N₂O and CO₂.—The direct ratio of the densities, referred to CO₂ = 44.002, that is, R = 44.002 L/L', has given experimentally the following values:—44.040 (Leduc), 44.020 (Rayleigh), 44.017 (Guye and Pintza).

The mean value is—

$$R = 44.025.$$

With the liquefiable gases, I have already indicated that the method of density-limits does not give the same accuracy as with the permanent gases; one can therefore confine oneself to calculating the value of the correction factor by the method of corresponding densities and by that of reduction to 0° of the critical elements, whence we have the following table (M = the corrected molecular weight of N₂O):—

TABLE XI.

Methods.	Correction factor.	M.	N.
Corresponding density: N ₂ O, 0° 760; CO ₂ , -4° 5/739 . .	1-0.00033	44.011	14.006
Reduction of the critical element . . .	1-0.00023	44.015	14.008
Mean . . .			14.007

The uncertainty ± 0.002 on the atomic weight of carbon is again reduced in this case to ± 0.001 on the atomic weight of nitrogen.

Corrected Ratio of the Densities of the Gases NO and O₂.—Gray has recently pointed out a preliminary value of the density of nitric oxide. From this is deduced for the weight of a normal litre L = 1.3402, which value is confirmed by experiments executed in my laboratory with the co-operation of Davila.

Taking for oxygen L = 1.4290 (mean of all the observations), the direct ratio is—

$$R = 32 \text{ L/L} = 30.012.$$

This value not being definitive, the correction factor has been calculated only by two methods; it is given in the following table, with the molecular weights M of NO, and the atomic weight N deduced from them.

TABLE XII.

Methods.	Correction factor.	M.	N.
Density limit (Jaquero and Schener) . . .	1-0.00020	30.006	14.006
Reduced to 0° of the critical element (Guye) . . .	1-0.00008	30.010	14.010
Mean . . .			14.008

Resumé of the Physico-chemical Values of the Atomic Weight of Nitrogen.—The preceding tables give rise to the following recapitulation of the means:—

Ratio.	N.
N ₂ : O ₂ (6 values) . . .	14.009
N ₂ : CO (6 values) [C = 12.002] . .	14.006
N ₂ O : CO ₂ (2 values) [C = 12.002] . .	14.007
NO : O ₂ (2 values) . . .	14.008

General mean . . . 14.008

The general mean of these four ratios of gas densities, corrected by physico-chemical methods, is therefore—

$$N = 14.008,$$

the greatest range being only 0.003.

In consigning this final value, which may be provisionally be rounded into 14.01, I must make the reminder that the method of density-limits has only been applied to the permanent gases.

With this reservation, one can but be struck with the agreement of the results, all the more remarkable that the experimental elements serving for the calculation of the correction factor have generally not been determined by the same experimenters as those to whom are due the values of the densities.

(To be continued).

THE

VOLUMETRIC ESTIMATION OF CYANATES.*

By A. C. CUMMING, B.Sc., and ORME MASSON, F.R.S.

THE want of a correct and convenient method for the quantitative analysis of solutions containing carbonate and cyanates led to the trial and adoption of the following convenient volumetric process.

To gravimetrically separate carbonate and cyanate from the solution of, say, the potassium salts, is apparently easy in the absence of cyanides and other complicating ingredients. The obvious method is to precipitate the carbonate with excess of barium nitrate, and then to throw down the cyanate from the filtrate by adding excess of silver nitrate. The BaCO₃ may be weighed as such, or as BaSO₄, and the AgCNO may be weighed on a tared filter, but is best dissolved in dilute nitric acid (thus eliminating any chloride that may be present), and precipitated for weighing as AgCl. In connection with such a separation the following points require notice.

J. W. Mellor (*Zeit. für Anal. Chem.*, xl., 19) stated that barium nitrate cannot be used for precipitating the carbonate from commercial cyanide solutions because barium cyanate is also insoluble, and he recommended the use of calcium nitrate. Others have since repeated the statement, and apparently it is accepted as true. Yet, on the face of it, it is extremely improbable that barium should form an insoluble cyanate; it is contradictory to the accounts of the salt given by Wohler and Berzelius (see "Watts's Dict.," Old Edition, ii., 193); and we have found it to be, as a matter of fact, quite incorrect, for numerous trials make it certain that Ba(CNO)₂ is not precipitated from cyanate solutions by addition of barium nitrate in the cold. We have, however, observed that when excess of barium hydroxide is employed (precautions being taken to exclude atmospheric CO₂) the clear filtrate from the carbonate slowly deposits a further precipitate; but this precipitate is not cyanate but carbonate produced from it by slow decomposition, probably according to the equation $\text{KCNO} + \text{Ba}(\text{OH})_2 + \text{H}_2\text{O} = \text{BaCO}_3 + \text{KOH} + \text{NH}_3$. Similar decomposition of Ba(CNO)₂ solutions is known to occur on boiling ("Watts's Dict.," *loc. cit.*); and it is probable

* Communicated by the Authors. From the *Proceedings of the Society of Chemical Industry of Victoria*, July–August, 1903.

that Mellor's statement that $\text{Ba}(\text{CNO})_2$ is insoluble is to be traced to this action. We find it quite unnecessary to substitute calcium nitrate for the barium salt, and we prefer the latter.

In either case, however, the precipitation of carbonate should be effected without heating, and the addition of ammonia or other alkali must be avoided, as this would lead to difficulties in the subsequent precipitation of silver cyanate. The question occurs, therefore, whether the carbonate precipitation is complete under these conditions. They are not the most favourable, but we believe that it may be taken as nearly, though not quite, complete, provided that a large enough excess of $\text{Ba}(\text{NO}_3)_2$ be used. The following tests were made with an approximately normal Na_2CO_3 solution, using the same quantity and the same total dilution in each case. The amount of reagent used was double the calculated quantity, except in the first precipitation with $\text{Ca}(\text{NO}_3)_2$, where it was somewhat less. A still larger excess should be used in practice, and probably gives more complete precipitation; but it appears that the results tend to be low, though barium nitrate is better than the calcium salt. Titrations of the solution with methyl orange and congo are given for comparison.

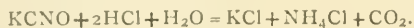
Normality of Na_2CO_3 Solution.

By titration { Methyl-orange .. 0.992 } Mean value, 0.990
 { Congo 0.987 }

By $\text{Ca}(\text{NO}_3)_2$ precipitation—(1) 0.986, (2) 0.937, (3) 0.923
 By $\text{Ba}(\text{NO}_3)_2$ precipitation—(1) 0.963, (2) 0.976

If a cyanate solution contain only normal carbonate, the filtrate from the barium precipitate is exactly neutral, and is in a fit state for the addition of AgNO_3 . If, however, any bicarbonate be present, the precipitation with $\text{Ba}(\text{NO}_3)_2$ is of course incomplete without the addition of ammonia, and it then becomes necessary to exactly neutralise the filtrate. This is troublesome, and apt to introduce errors. Excess of NH_3 would dissolve AgCNO , while any free acid would decompose some of the cyanate; and of course free caustic alkali must be avoided as it would precipitate silver oxide. Another objection to the determination of cyanates as AgCNO is that this precipitate is sometimes contaminated with reduced silver, though this is not always the case. Under favourable conditions, however, it may be taken as giving correct results, as it has been shown by Walker and Hambly (*Trans. Chem. Soc.*, lxxvii., 747) that AgCNO is practically insoluble in water containing excess of AgNO_3 , and may be washed with but little loss.

Apart from the faults of the gravimetric process, it is obvious that a volumetric method is preferable where frequent analyses have to be made, provided that a sufficiently accurate one is available. We have found the following method satisfactory so far as it has been yet tested. It depends on the fact that cyanates are, as such, neutral to indicators, but that when boiled for a short time with excess of dilute mineral acid they neutralise a part of it, being quantitatively converted into CO_2 , which escapes, and salts of the metal and ammonia,—



Allen describes ("Commercial Organic Analysis," vol. iii., Part III., p. 484), and others have recommended, an analytical method in which the insoluble AgCNO is similarly used to neutralise standard nitric acid; but, so far as we know, the following process, which depends primarily on the neutrality of soluble cyanates as such, is novel.

It may be briefly described thus:—A known volume of the mixed carbonate and cyanate solution is first titrated in the cold with standard acid, using methyl-orange or congo indicator. It is important to use a neutral solution of the indicator for comparison, and to record the exact point when the first change of tint is observed, for the decomposition of cyanate by excess of acid makes accurate back titration impossible. After thus obtaining the measure of the carbonate, a sufficiently large measured excess of the

acid is run in, when it will be seen that there is (as a consequence of the above reaction) a long range of neutral tint, only gradually deepening to the true acid colour. The mixture is then boiled for a few minutes to ensure the complete decomposition of the cyanate and to expel the CO_2 . The boiling may be stopped when bumping sets in, and the solution is cooled, and more indicator added if necessary. The residual excess of acid is now determined by titration back with standard alkali. If we call this residual excess n^1 , and the original added excess n , it is obvious from the equation for the decomposition of cyanate by acid, that $\frac{1}{2}(n - n^1)$ is the measure of the cyanate.

A second and independent measure of the cyanate may be obtained as follows:—After the last-mentioned titration, a sufficient excess of the alkali is run in, and the mixture is now boiled till all the ammonia has been expelled. The mixture is cooled, given additional indicator if necessary, and titrated back with acid, so as to determine the residual excess of alkali. If we call this residual excess m^1 , and the original added excess of alkali m , $m - m^1$ is the measure of the quantity of NH_3 expelled. This is of course equivalent to the cyanate, unless the original solution contained ammonium salts. In such a case $(m - m^1) - \frac{1}{2}(n - n^1)$ gives a correct measure of their amount. It may be here mentioned that in the methods described by Herting (*Journ. Soc. Chem. Ind.*, Abstracts, xx., p. 838) and Milbauer (*Journ. Soc. Chem.*, Abstracts, 1903, ii., p. 392), for the analysis of commercial cyanide solutions, the cyanate determination is based entirely on the amount of ammonia present after boiling with acid, and that they are therefore necessarily misleading if, as sometimes happens, the cyanide contains NH_4 salts. In working our method we employ decinormal sulphuric acid and soda, and the analysis is done simultaneously in duplicate.

The following tests were made with a solution of potassium carbonate and cyanate, prepared by careful addition of red lead to fused KCN. The solution contained a trace of KCN, which was determined by titration with AgNO_3 , and allowed for in calculating the results. The gravimetric determinations of carbonate and cyanate, obtained by the methods already discussed, are given for comparison.

Analysis of Solution of K_2CO_3 and KCNO .

(Results stated in grm.-equivalents per litre).

I. Gravimetric Analysis.

Carbonate (by precipitation with barium nitrate):—(1) 0.0178, (2) 0.0151, (3) 0.0165, (4) 0.0168, (5) 0.0177. Mean, 0.0168.

Cyanate (by precipitation with silver nitrate):—(1) 0.0429, (2) 0.0413, (3) 0.0420, (4) 0.0439, (5) 0.0425. Mean, 0.0425.

II. Volumetric Analysis.

Carbonate (titration in the cold):—(1) 0.0182, (2) 0.0181, (3) 0.0181, (4) 0.0182. Mean, 0.0182.

Cyanate (titration after acid boiling):—(1) 0.0440, (2) 0.0430, (3) 0.0429. Mean, 0.433.

Cyanate (titration after alkaline boiling):—(1) 0.0412, (2) 0.0429, (3) 0.0406, (4) 0.0414. Mean, 0.0415.
 Mean of all volumetric results for cyanate, 0.0424.

Obviously, the volumetric method here described has but limited scope, unless it can be used in the analysis of commercial cyanide.

(To be continued).

Sixth International Congress of Applied Chemistry—Rome, 1906.—The Sixth International Congress of Applied Chemistry will be held in Rome in April, 1906, during Easter week. All communications should be addressed to the General Secretary, Prof. Vittorio Villavecchia, Via Panisperna 89, Rome.

THE CHEMICAL SEPARATION OF THE RADIO-ACTIVE TYPES OF MATTER IN THORIUM COMPOUNDS.*

By HERMAN SCHLUNDT and RICHARD B. MOORE.

OUR knowledge of the nature of the radio-activity of thorium is largely due to the extensive researches of Rutherford and Soddy (*Journ. Chem. Soc.*, 1902, lxxxi., 131, 837). These investigators have shown that the radio-activity of the ordinary thorium compounds on the market consists of four parts, due to four specific types of matter. On the basis of their theory of successive disintegration, the parent thorium is slowly but constantly undergoing change. A very small fraction of the thorium atoms is continuously breaking up, giving off α -particles and leaving a new type of matter, Thorium X, which is also radio-active. Thorium X, in disintegrating, gives rise to a radio-active gas, the Emanation, which breaks up rapidly, sending out particles and depositing a solid on near-by objects. This solid likewise emits radiations and is therefore responsible

Rutherford and Soddy have succeeded by chemical means in removing from thorium compounds the matter causing the major part of the radio-activity. The thorium, however, still retains some activity, and within a month it recovers its normal equilibrium value. During the same time the separated non-thorium types of matter rapidly lose their radio-activity, and at the end of a month are comparatively inactive. (Compare curves A, a; Plate I.)

The separation of ThX from thorium consists in precipitating thorium as hydroxide from an aqueous solution of the nitrate by means of dilute ammonia, added in excess. The filtrate, free from thorium, after evaporation and ignition to remove ammonium salts, yields a minute residue of intense activity compared with that of the original thorium, weight for weight. The precipitate, although containing all the thorium, possesses no emanating power at first, and its activity is less than half of its original value. The matter causing the imparted activity, being insoluble in dilute ammonia solutions, is found in the precipitate. When thorium is precipitated as carbonate, oxalate, or phosphate, the residues obtained from the filtrates are inactive and the precipitates show no loss of radio-activity. In fact, ammonium hydroxide was the only reagent of those tried by Rutherford and Soddy which

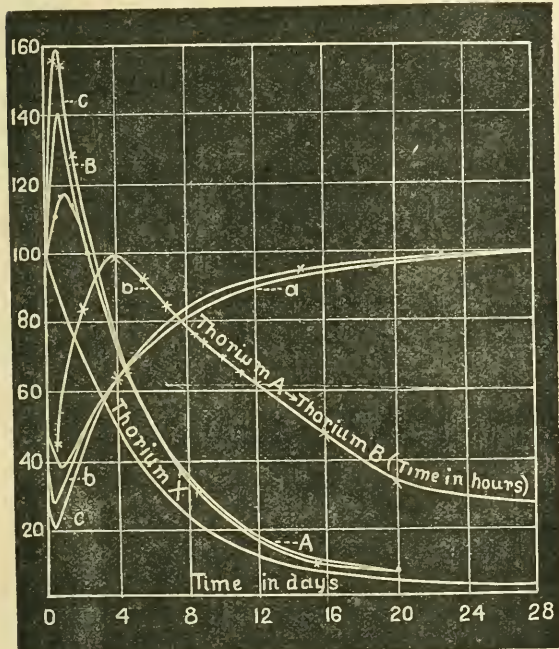


PLATE I.

Ammonia, A a; Pyridine, B b; Fumaric acid, C c,

for the temporary radio-activity exhibited by bodies left in the neighbourhood of thorium compounds. The successive changes — Thorium $\Rightarrow$ Thorium X $\Rightarrow$ Emanation $\Rightarrow$ Matter† causing imparted or excited activity $\Rightarrow$ The final product—go on simultaneously in thorium compounds, and the radio-activity ordinarily observed represents the combined effect of these different types of matter. According to Rutherford ("Radio-activity," p. 307), each of the components supplies approximately an equal proportion of the total activity. Thorium X and its disintegration products, however, constitute but an infinitesimal amount of the total quantity of matter, but their rate of transformation is immense in comparison with that of thorium.

* From the *Journal of Physical Chemistry*, ix., No. 8, p. 682.

† This type has been shown to be complex. Cf. Rutherford, *Phys. Zeit.*, 1902, 254; *Phil. Mag.*, 1903, [6], v., 95; von Lerch, *Drude's Ann.*, 1903, xii., 745; Pegram, *Phys. Rev.*, 1903, xvii., 424. This product is variously designated by different writers as the induced activity, the excited activity, the imparted activity, and a component of the secondary activity.

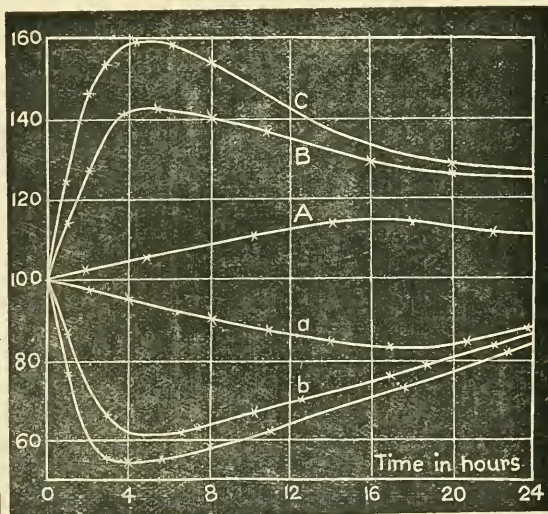


PLATE II.

separated ThX from thorium compounds, thus showing that ThX is insoluble in aqueous solutions of the reagents ordinarily used for precipitating thorium. With the view of arriving at other methods of separation we jointly undertook some experiments with thorium compounds, and, although work is still in progress, a report on some of the methods by means of which a separation is obtained may be of interest. In connection with this work we found a method of separating, by chemical means, the matter causing imparted activity from the other components, and these experiments are included in this paper.

Separation by means of Pyridine.

In the course of the preliminary experiments it was found that the separation of ThX from thorium is readily carried out by means of pyridine. When pyridine is added in excess to a dilute aqueous solution of thorium nitrate, no precipitate forms at room temperatures, but upon heating the solution, the thorium is completely precipitated as hydroxide (Miss Jefferson, *Journ. Am. Chem. Soc.*, 1902, xxiv., 545). The filtrate, after evaporation and ignition in order to expel the pyridine nitrate, yields a very slight residue which was found to be highly radio-

active. Its rate of decay is the same as that of ThX, its activity falling to half value in approximately four days.

Two samples of pyridine from Merck were used in these experiments. One was marked "free from homologues," and the other was the medicinal grade. The samples were re-distilled, the former passing over between 114.5°—115.5°, the latter between 114°—118° under a pressure of 748 mm. The two samples exhibited no specific difference in their action with the thorium solutions. Three twenty-grm. samples of thorium nitrate, obtained from Eimer and Amend, New York, were used in the course of the experiments. A composite of each sample was prepared by pulverising it rapidly in an agate mortar. Subsequent hydration was guarded against, so that the small samples used in the separations should contain the same percentage of thorium. The nitrate upon ignition lost 51.3 per cent. in weight. Assuming that the sample was pure thorium nitrate, the calculated amount of water of hydration present was approximately 3.5 molecules per molecule of nitrate.

Some experiments were carried out for the purpose of ascertaining the conditions favourable for the separation of ThX by means of pyridine. Within a wide range the dilution of the thorium nitrate solution has little or no effect on the separation. Solutions varying in strength from 0.1 to 10 per cent, and containing the same amounts of thorium, yielded filtrates free from thorium, which after evaporation and ignition possessed approximately the same activity. For complete precipitation of the thorium the pyridine must be added in excess. The addition of pure pyridine gave the same results as an aqueous solution of the reagent. Boiling coagulates the gelatinous precipitate and causes it to settle rapidly. In one case the precipitate was boiled for half an hour, with an excess of pyridine in a flask fitted with a reflux condenser. The residue from the filtrate, however, did not differ materially in activity from the residue of another sample precipitated at the same time from a hot solution without boiling. Not all of the ThX in the sample is removed by one precipitation with pyridine. In removing ThX by means of ammonia, Rutherford and Soddy found that three successive precipitations were necessary to free thorium completely from ThX. The same holds true for the removal of ThX by means of pyridine. By dissolving the precipitate in hot dilute nitric acid and then re-precipitating the thorium with pyridine, as rapidly as possible, so that the ThX produced in the precipitate shall not become appreciable, residues were obtained from the successive filtrates with activities 100, 7.7, and 1.0 respectively. In three successive precipitations with ammonia, Rutherford and Soddy obtained residues whose activities were in the ratio of 100, 8, and 1.6 respectively, and in one of our experiments in which three successive precipitations with ammonia were made, the activities of the residues obtained were 100, 9.1, and 1.0 respectively. In several instances, however, the activities of the residues obtained from the second and third filtrates were considerably greater with both pyridine and ammonia than the values cited, although the conditions under which the precipitations were made were apparently the same.

The amounts of thorium nitrate used in the different experiments ranged from 0.2 to 1.0 gm., but as a rule a known weight of the nitrate was taken. With amounts greater than 0.2 gm. a suitable fraction of the filtrate was evaporated, platinum dishes being used for the most part. The precipitate was dried, together with the filter paper, on a hot iron plate. The greater portion was then removed from the paper and the latter incinerated. Ashless filter paper was always used. The entire precipitate was then transferred to a mortar and ground up under 95 per cent alcohol.* The contents of the mortar were next poured out upon shallow, circular, metal dishes, 12 c.m. in diameter. Particles of the precipitate adhering

to the mortar were washed out with alcohol, and the latter was removed by setting fire to it. A thin layer of thorium oxide, of nearly uniform thickness, was obtained in this way, which adhered sufficiently to the dish to prevent shifting of the powder in transferring it to and from the testing apparatus for the subsequent measurements of radio-activity. The amount of thorium oxide spread out on one of the dishes was approximately 0.1 gm.

The radio-activity of the precipitates and residues was determined by the electrical method, the Dolezalek type of quadrant electrometer being employed. When the needle was charged to 100 volts, a difference of potential of one volt between the two pairs of quadrants produced a deflection of 280 divisions on a millimetre scale, one metre from the mirror. The directions given by Rutherford in his book on "Radio-activity," for the measurement of ionisation currents by means of the quadrant electrometer, were found very helpful.

The testing apparatus consisted of a cylindrical vessel of galvanized iron, 15 c.m. in diameter and 30 c.m. high, supplied with an insulated central brass rod, to the lower end of which a circular disc 8 c.m. in diameter was soldered. The vulcanite insulator, carrying the central electrode, was provided with a guard ring to prevent leak across the insulation. The guard ring was kept earthed during the tests and was insulated from the testing vessel by means of sulphur and sealing-wax. The lower open end of the testing vessel fitted into a circular groove in a wooden base covered with thin sheet copper, and supported by vulcanite legs. The groove contained about 0.5 c.m. of mercury, which served as a seal. A potential of 150 volts applied to the testing vessel was found sufficient for obtaining saturation values for the ionisation currents measured. The electrometer, testing vessel, and connections were screened from external electrical disturbances by placing them in a cage of wire netting which was well earthed.

The connections were made in the usual way. One pole of a water battery of 156 cells was earthed, the other was connected to the outside of the testing vessel. From the central electrode of the latter a wire connected with one pair of quadrants of the electrometer, the other being earthed. The central electrode of the testing vessel also had an earth connection which was broken, when readings were made, by means of a special switching device (*Journ. Phys. Chem.*, 1905, ix., 324).

In measuring the radio-activity of the precipitates and residues, readings were made at short intervals—usually about an hour—during the first twelve hours after separation. Subsequently, measurements were made at intervals of gradually increasing length for a period of a month, at the end of which time the activity of the precipitate had acquired a constant maximum value, while the residue from the filtrate had become completely inactive. Between tests the dishes containing the samples were covered loosely with watch-glasses, and care was taken to disturb them as little as possible during the progress of their decay and recovery. On account of the emanation, equilibrium was often not established in the testing vessel for several minutes after the sample was introduced. The plan followed was to make readings until constant values were obtained. The effect due to the emanation was then determined by covering the sample with two thicknesses of ordinary paper, which cuts off nearly all the α -radiation (Rutherford and Soddy, *Journ. Chem. Soc.*, 1902, lxxxi., 837). The difference between the values calculated from the two readings was taken as the activity of the sample. The air-leak of the apparatus, about 25 m.m. divisions per minute, was deducted from the values found. As the measurements for any pair of samples usually extended over a month, and as slight changes in the sensitivity of the apparatus occurred, it was found necessary to employ the usual standard of uranium oxide in order to ascertain the corrections to be made in connection with the readings due to such changes.

In carrying out two parallel separations with ammonia

* The suggestion for this method was obtained from the work of McCoy on uranium (*Journ. Am. Chem. Soc.*, 1905, xxvii., 4).

and pyridine by three successive precipitations with each reagent and using the same weight of thorium nitrate, it was invariably found that the filtrate from the sample precipitated with pyridine gave a residue of greater activity than the filtrate residue from the sample precipitated with ammonia, while the activity of the precipitate was correspondingly less than that of the precipitate obtained with ammonia. These differences in activity were found to be due to the matter causing imparted activity. When thorium is precipitated with ammonia, Rutherford and Soddy found that the matter causing imparted activity is insoluble in dilute ammonia, and hence is found in the precipitate. When the separation is made by means of pyridine the matter causing imparted activity remains in solution—in part, at least, as the following experiment shows:—ThX was removed from thorium by three successive precipitations of a dilute aqueous solution of thorium nitrate with ammonia. The residue obtained by evaporating that portion of the filtrate given by the third precipitation, was tested for radio-activity and found to contain only about 1 per cent of the activity of the residue obtained by evaporating the filtrate from the first precipitation, thus showing that the ThX had been practically all removed. The thorium hydroxide precipitate, free from ThX, was at once re-dissolved in hot dilute nitric acid, rapidly re-precipitated with pyridine, and the precipitate filtered off by means of a suction-pump. The filtrate, after evaporation and ignition, gave a very minute residue, which was found to be radio-active. It was identified as the matter causing imparted activity by its rate of decay, its activity falling to half value in eleven hours.

Four successive precipitations then—three with ammonia and one with pyridine—separate ThX and a portion of the matter causing imparted activity.

(To be continued).

PROCEEDINGS OF SOCIETIES.

FARADAY SOCIETY.

Ordinary Meeting, December 12th, 1905.

Mr. JAMES SWINBURNE, Vice-President, in the Chair.

Mr. J. SWINBURNE and Dr. G. RUDORF presented a paper on "*The Physics of Ore Flotation*." (See CHEMICAL NEWS, vol. xcii., p. 288).

Prof. A. K. HUNTINGTON then read a paper on the same subject entitled "*The Concentration of Metalliferous Sulphides by Flotation*." The paper also embodies the author's contribution to the discussion on the previous paper.

The paper has reference to the flotation processes of Potter and Delprat, which have been successfully applied in practice to the further concentration of the "tailings" obtained in the treatment of the sulphide ores of the Broken Hill district. These ores consist of sulphides of lead and zinc carrying silver, with a gangue composed of quartz, rhodonite, garnets, and small quantities of carbonates.

The flotation process consists in adding to the tailings dilute sulphuric acid (Potter), or a solution of acid sulphate of soda (Delprat) at about 65° C. Under these conditions the metallic sulphides are floated up by attached bubbles of gas, and form a coherent scum which can be removed, leaving behind the gangue, the separation being practically a quantitative one.

Experiments are described which prove that the gas causing flotation is CO₂ derived from native carbonates of iron and manganese present in the ore, and not from calcite or from carbonates produced on the surface of the sulphides by weathering. Carbonates which are decomposed by dilute sulphuric acid in the cold do not give rise to the formation of a scum.

Experiments are also described showing that the gas escaping during flotation carries an electrical charge, leaving an opposite charge on the solution. Electrometer determinations of the charge were made, but it was not found possible to establish a direct connection between the electrical phenomena and the fact of flotation. No change in the surface tension conditions of the solution in contact with a metallic sulphide is to be observed on electrification.

The assumption of Messrs. Swinburne and Rudorf of the presence of an air-film on the surface of the sulphide particles is criticised, and it is shown that the particles are floated perfectly after precautions have been taken to remove any adherent film of gas by exhaustion with acid, washing with alcohol, treatment with air-free distilled water, and exhaustion with the pump, &c. Flotation depending on the presence of an adhering film of air is made use of in certain suggested concentration processes, which, however, are different in principle from those under consideration.

It is a curious fact that specimens of zinc blende containing but little gangue, which do not form a scum on treatment with sulphuric acid and carbonate of iron, give an excellent flotation if previously mixed with sand. On the other hand, too great dilution with inert matter injures the flotation. The Broken Hill vanner tailings appear to be ideally suitable for the flotation process. These experiments dispose of Messrs. Swinburne and Rudorf's contention that blende scarcely floats at all, and incidentally of the statement that "zinc blende is thus easily raised by galena when intimately associated." They themselves admit that galena has to be very finely pulverised to float successfully; it is difficult therefore to see how it could be expected to float with attached inert blende. It appears more probable that the blende helps the galena to float. This view was strengthened by some experiments made on the wetting of sulphide surfaces.

The degree of wetting of a surface may be judged by measuring the angle which the liquid makes with it. Direct determinations of this angle for different minerals by a goniometer method are described, the values obtained varying from 47 to 63° for different sulphides. Quartz and magnetite are completely wetted by water. Alcohol wets all sulphides, but on again placing in water the apparent "greasiness" is restored.

When a gas bubble comes into contact with a mineral particle, the extent of surface of the bubble which will be in contact with the solid depends on the angle of contact of the solid with the liquid. If the angle is such as to cause a relatively large surface of the gas to be in contact with the solid, and the bubble is sufficiently large, the particle will be floated. The less the wetting the greater will be the force required to detach the bubble. If the surface of the solid is wetted, the bubble has no attachment at all. The different conditions met with are illustrated by means of diagrams.

Mr. BERTRAM BLOUNT said, although unable to put forward a satisfactory theory of his own, he was unconvinced by those proposed by the authors. Nor did their theories help in practice, for the only way to discover whether the flotation process could be applied to a particular ore was by experiment.

Mr. J. G. A. RHODIN thought that the crux of the theoretical difficulty was to discover how the gas bells were able to break through the liquid surface-films on the solid particles so as to come into contact with the latter; once that was known, Quincke's formula for triple contact of gas, liquid, and solid, could be applied. The key to the problem lay in the application of the law of mass-action, the necessary condition being that the solid must partly go into solution. The occluded or condensed gases which it is practically impossible to remove from the surface of a solid helped the action.

Dr. O. J. STEINHART referred to oil separation processes. He also pointed out that no separation process could be considered entirely satisfactory which did not separate galena from blende.

Mr. S. F. SPIERS described some measurements of the Volta effect between metals in so-called *vacuo*, which illustrated the difficulty, if not impossibility, of removing condensed air-films from the surfaces of solids.

Dr. F. MOLLWO PERKIN remarked on the differences between occlusion and surface-condensation of gases.

Mr. N. J. BLUMAN said that the theories put forward did not explain the selective action of the air-bubbles.

Mr. R. FREDERICK YORKF thought that an electrostatic theory would be required to explain the selective action.

Dr. H. BORNS hoped that more experiments would be made so as to explain some of the anomalous effects observed by Professor Huntington.

Dr. G. RUDORF said that Mr. Swinburne and he did not claim "weathering" as absolutely essential. With reference to the contact angle made by a liquid with a solid, that itself depended on the air-film.

Mr. J. SWINBURNE said that the essential point which the theory Dr. Rudorf and he had put forward was the temperature effect. No theory could explain the differences in the action on the different constituents of the ore any more than one could the differences of specific gravity; these depended on the varying inherent properties of matter. The presence of an air-film was not necessary, if the particles to be lifted were "greasy."

Prof. J. WALKER, F.R.S., contributed a paper on "*The Ions of Pure Water*."

In the discussion on Dr. Lowry's paper, on "*An Application to Electrolytes of the Hydrate Theory of Solution*," Mr. Bousfield drew attention to an apparent discrepancy between the temperature coefficient of the mobility of hydrogen and hydroxide ions on the one hand, and the temperature coefficient of the conductivity of water on the other. The author points out that water for which the data used by Mr. Bousfield holds good owes its conductivity almost wholly to impurity, and that Mr. Bousfield in his theoretical deduction has neglected the effect of temperature on ionic concentration. When the data obtained by Kohlrausch for pure water are employed, and when allowance is made for the temperature coefficient of ionisation, the discrepancy vanishes.

Mr. W. R. BOUSFIELD (communicated) said that he did not profess to be dealing with *pure* water, but with "water" in inverted commas. But he agreed now that there was strong evidence that pure water had a genuine conductivity due to H and HO ions.

NOTICES OF BOOKS.

Radio-activity. By E. RUTHERFORD, D.Sc., F.R.S., F.R.S.C. Second Edition. Cambridge: The University Press. 1905.

THE text of the most recent edition of this work has been extensively enlarged and re-arranged, the rapidity with which our knowledge of the subject is widening rendering it necessary almost to re-write the whole. At the same time, considering the imperfect state of development of the subject, it is especially noticeable how very seldom the author's predictions in the first edition have had to be corrected in accordance with increased knowledge, and how remarkably some of the theories he put forward have been verified. As a case in point, we may mention the disintegration theory, which has proved to be of the greatest value in explaining and interpreting the relations between the properties of the various radio-active substances. The new matter which has been added to the book relates specially to the theory of successive changes, which is treated fully in three fresh chapters, in which the mathematical theory is discussed very lucidly, and the results obtained by mathematical analysis are applied to explain the radio-active phenomena in the case of the elements uranium, radium, thorium, and actinium, and their products.

A large amount of new material dealing with the properties of the radiations and emanations has also been given a place in the book, and, in fact, besides the new chapters mentioned above, the last three chapters have been almost entirely re-written, while considerable alterations have also been made in the earlier parts. The book contains an admirable exposition of the subject, and will be found quite invaluable by those who are interested in the new science; they will find it full of the very latest information, while it need hardly be said that all theories are critically discussed by the author in the most unbiassed spirit.

The Laboratory Book of Dairy Analysis. By H. DROOP. RICHMOND, F.I.C. London: Charles Griffin and Co., Ltd. 1905.

THIS book contains very explicit and practical directions for the analysis of milk, butter, and cheese, and although we should not recommend the untrained novice to attempt to embark upon technical analysis, he would undoubtedly find this work a very safe guide, and with its aid he might be able to ascertain a good deal of valuable information about the quality and condition of the above dairy products. This, however, applies only to the simpler tests, the more difficult being described in technical language for the benefit of the experienced chemist only. In some cases the experimental directions for these more difficult tests might with advantage have been made somewhat fuller; for instance, it seems doubtful whether the instructions relating to the estimation of sugar by the polarimetric method would enable any one who was not already fairly conversant with its working to perform analyses. Speaking generally, however, the author has given careful attention to the details of manipulation, and the pages on the application of analytical methods to the solution of problems give a useful though slight account of the various problems with which the dairy chemist may be confronted. The treatment of butter and cheese is rather less full than that of milk, but instructions are given for the performance of complete ordinary analyses of both substances.

Terrestrial Magnetism and its Causes. By F. A. BLACK. London: Gall and Inglis. 1905.

THIS book puts forward a new theory to explain the fact that the earth is a magnet. Adopting the hypothesis that the space surrounding the earth, beyond its atmosphere, is permeated by a medium of an electrical nature, the author suggests that waves of this medium are impacted against the earth, each portion of which in consequence of its diurnal movement passes under these electric waves, and thus a "sheet of electrical influence" surrounds the earth, which is therefore magnetised by electric induction. Here, of course, a difficulty at once suggests itself, viz., that the magnetic poles should by this theory be identical with the orbital poles, which is not the case, and the author, fully aware of this objection, devotes a large portion of his book to proving that the magnetic poles describe a diurnal revolution resembling that of the orbital poles. It seems to us, however, that the author in this connection is too ready to adopt probabilities and likelihoods in place of established facts, and although he has collected and sifted a large amount of material bearing upon the magnetisation of the earth, we cannot see that he has really forwarded the elucidation of the question. The book is obviously the result of careful work undertaken from a genuine love of the subject, and as such deserves the attention of those who are devoting themselves to endeavouring to solve this complicated problem.

Zur Kenntniss der Kupfer-Zinklegierungen. ("A Contribution to Our Knowledge of the Copper-zinc Alloys"). By Dr. OTTO SACKUR. Berlin: Julius Springer. 1905.

THESE papers, which are reprinted from the *Arbeiten aus dem Kaiserlichen Gesundheitsamte*, contain detailed ac-

counts of the work which the author, assisted by Dr. P. Manz and Dr. A. Siemens, has done in reference to the question of the behaviour of metallic alloys towards acid liquids. The thorough investigation of this subject, which is one of great importance both from the scientific and hygienic standpoints, has brought to light some interesting new facts concerning the constitutions, solution pressures, and other physical properties of the alloys of lead with tin, and copper with zinc. The work on the former alloys has already been published, and is therefore given only in outline in this volume, while the copper-zinc alloys are treated more fully; from the investigation of these latter the author establishes the conclusion that zinc and its alloys with copper are passive in many solutions.

Nouvelles Méthodes Générales d'Hydrogénation et de Dédoublément Moléculaire. ("New General Methods of Hydrogenation and of Molecular Condensation"). By PAUL SABATIER and J. B. SENDERENS. Paris: Gauthier-Villars. 1905.

THIS small volume contains a detailed exposition of the authors' investigation of general methods of hydrogenation by means of reduced metals, describing the apparatus and experimental procedure, and discussing the principal results obtained. The metals employed include nickel, cobalt, iron, and copper, and by means of them many reactions have been induced; nickel and copper reduced from their oxides being specially active in this respect. These reactions, moreover, generally occur without any alteration in the appearance of the metal, which acts as a catalyser. In some cases the hydrogenation constitutes a complex chemical phenomenon; for instance, the hydrogen replaces oxygen, eliminated as water, or the halogens, eliminated as hydro-acids. The most important new method among the many transformations thus affected which the authors discuss, is perhaps the action of gaseous hydrogen in presence of reduced nickel upon volatile substances at temperatures above 250°. Numerous condensations are similarly produced, and the authors have arrived at somewhat unexpected results in the case of acetylene, from which they have obtained liquids closely resembling natural petroleum.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 23, December 4, 1905.

Action of Silicon on Pure Aluminium, on Impure Aluminium. Silico-aluminides.—Em. Vigouroux.—The author investigates the condition of the silicon found in alloys of silicated aluminium, and particularly the nature of the metallic cement in which silicon crystallises when aluminium is allowed to act in excess on silicated substances, *i.e.*, silica, fluorides, &c. Does the aluminium remain as such, or is it converted into silicide? He maintains that the silicide is not formed, for, on treatment with hydrochloric acid, aluminium chloride, hydrogen, and crystallised silicon are obtained instead of amorphous silicon. In the gas liberated from this reaction there is no siliciuretted hydrogen, and the presence of silica in small quantities in the liquid will be explained later. And, finally, the brown particles found in the solid residue, although apparently amorphous, can be shown by the microscope to be crystallised silicon. In the case of impure alloys of aluminium the results are quite different. Combustion can take place, due to the presence of a third element in the impurity, with the formation of compounds which the author calls "silico-aluminides." He was led to the discovery of these new bodies while trying to form crystalline silicides without the use of free silicon. By heating the double fluoride of potassium and silicon with aluminium in known proportions with a small quantity of the oxide of the alloying metal, cooling, and then

alternately treating the residue with hydrochloric acid and soda to destroy the free aluminium and silicon, the author obtained a silico-aluminide. In this way he has obtained silico-aluminides of iron, nickel, cobalt, chromium, manganese, molybdenum, tungsten, vanadium, uranium, titanium, &c., but has not succeeded, up to the present, in getting those of lead, tin, antimony, and bismuth. He then proceeded to determine three different methods of preparation, of which he gives details. As to the general properties of the silico-aluminides, they are comparable to the silicides; they have a metallic lustre, they are heavy, hard, brittle; their crystalline forms are often very definite. A certain number can be melted in the reverberatory furnace in a current of hydrogen. Acids attack a certain number, with the formation of silica, but most of those studied are not acted upon by acids, however concentrated, except by hydrofluoric acid. All resist the action of alkalis in solution. The author's conclusions are as follows:—1. Silicon and aluminium, unable to combine in the pure state to form silicides of aluminium, often combine in the presence of a third metal, forming silicides of aluminium and that metal; in other words, silico-aluminides, definite crystalline bodies. 2. The knowledge of the cases in which these compounds are formed leads one to the rejection of any clay derivative as a recipient in all cases of preparation of metals susceptible to the formation of silico-aluminides, and explains why metals like vanadium, uranium, titanium, &c., have not been separated in a state of purity.

On Decahydronaphthol- α and Octohydride of Naphthalene A.—Henri Leroux.—1. *Decahydronaphthol- α* , $C_{10}H_{17}OH$.—When naphthol- α is hydrogenated below 200°, and the liquid mixture passed several times through a nickel tube, crystals are obtained which, after repeated crystallisation from petrol ether or acetone, give decahydronaphthol- α . This compound appears as fine colourless needles, melting at 62°, slightly soluble in water, but readily in the usual solvents. It distils at 230° at ordinary pressure without decomposing, and volatilises at 100° under 12 m.m. pressure. Heated in the presence of phosphoric anhydride, anhydrous oxalic acid, or fused bisulphate of potassium it loses one molecule of water, forming octohydride of naphthalene. *Octohydride of Naphthalene A*.—This compound the author provisionally calls octohydride of naphthalene A, formed from the dehydration of the α -decahydronaphthol, reserving the letter B for that obtained from the β -compound. It is a liquid distilling between 195° and 200°, mixed with decahydronaphthol- α . By treating an ether solution of the mixture with sodium, the decahydronaphthol forms an insoluble sodium derivative, which is easily separated off. By distilling off the ether, the pure carbide is left behind. It is a colourless liquid boiling at 190–191° at ordinary pressure; its density is 0.931 at 0° and 0.914 at 17°. The index of refraction for the D line is 1.4993 at 17°, corresponding to a molecular refraction of 43.71. The calculated index is 43.52.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Fruit Essences—Can any reader supply information as to the best works on the subject of the compounding of essences for the manufacture of non-intoxicating beverages?—N. E.

MEETINGS FOR THE WEEK.

- MONDAY, 8th.—Society of Chemical Industry, 8. "Cinchona Barks and their Cultivation," by D. Howard. "New Method for the Quantitative Estimation of Acetone," by S. J. M. Auld.
- TUESDAY, 9th.—Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Astronomy," by Prof. Herbert Hall Turner, D.Sc., F.R.S.

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THE CHEMICAL NEWS.

Vol. XCIII., No. 2407.

NEW RESEARCHES ON THE ATOMIC WEIGHT OF NITROGEN.*

By PHILIPPE A. GUYE.

(Continued from p. 5).

IV. *New Gravimetric Methods for Controlling the Atomic Weight of Nitrogen may take the place of the Classical Methods. They already admit of Determinations to a Unit of the Second Decimal place of the Atomic Weight of Nitrogen, and Confirm the Results of the Physico-chemical Values.*

HAVING proved that the chemical gravimetric methods are not capable of sufficient accuracy for determining the atomic weight of nitrogen to a unit in the second decimal place, and having also brought forward the remarkable agreement of physico-chemical methods applied to nitrogen, I considered that the conviction of chemists would only be satisfied with regard to this subject when the value $N = 14.01$ should have also been obtained by purely gravimetric methods.

The classical methods of Stas not yielding the desired degree of accuracy, it was essential to renew the study of this question by absolutely new methods, based upon the reliance of the atomic weight of nitrogen as directly as possible upon that of oxygen. In other words, it was necessary to revert to simple and rational methods, systematically discarding all indirect methods. The history of the determination of the atomic weights is rich in achievements of this kind; it will suffice to recall at this point the discovery by Dumas and Stas (1841) of an error of 2 per cent in the atomic weight of carbon, as fixed by Berzelius. The exact determination of two simple ratios— $C : CO_2$ and $CO : CO_2$ —by de Saussure's method was more conclusive than the numerous analyses of organic compounds previously carried out by the most famous chemists of their day.

Thus the problem reverts to the attempt to analyse accurately the oxygen compounds of nitrogen, which the best experimenters have generally regarded as impossible of exact execution. The difficulty of preparing these gases in the pure state is without doubt the chief reason that so far no attempt of the kind has been carried out. The researches undertaken in my laboratory since 1902 to attempt to fathom this abyss have proved that the difficulties are serious but not insurmountable, above all with the progress gained in technique relative to the manipulation of the gases. The results already obtained, it is true after many fruitless experiments, lead to absolutely conclusive numbers, which confirm the physico-chemical values.

Under these circumstances there is no doubt, either in the mind of my fellow-workers or in my own, that the improvements, which will finally be added to the new methods I am about to describe, will re-affirm the agreement of the physico-chemical and gravimetric values of the atomic weight of nitrogen.

In the first place, we embarked on the problem of the exact analysis of nitrous oxide, N_2O . This choice was chiefly influenced by three considerations:—

The first was inspired by the fact that the determinations of the exact density of this gas by different observers has given concordant results; this was a favourable presumption of the possibility of obtaining this body in a pure state.

The second was drawn from the high percentage of nitrogen in the sub-oxide, the highest among the oxygen

compounds of nitrogen; for the same accuracy, the atomic weight of nitrogen deduced from analysis of an oxide of nitrogen is more certain in proportion to the percentage of nitrogen contained in the oxide.

The third is based upon the fact, worthy of note, that the discussion of the causes of error in the experimental methods adopted, tends to prove that the value of the atomic weight of nitrogen thus obtained should be rather too great than too small. This point was of importance in view of the nature of the question under consideration.

The choice of nitrous oxide being settled, its analysis was effected in two ways—(a) gravimetrically, (b) volumetrically. The first experiments were made with the co-operation of Bogdan. Jaquered and Bogdan also carried out the volumetric analysis.

Gravimetric Analysis of Nitrous Oxide.—This analysis was carried out by decomposing a known weight of the oxide by means of red-hot iron; the increase of the weight of the iron gave the weight of oxygen contained. It would take too long to enter into all the details of the experiment; I will confine myself to mentioning a few characteristic features.

In order to avoid the causes of error arising from the weighing of large bulbs, the nitrous oxide was weighed in the condensed condition in charcoal; one can thus work with small pieces of apparatus.

The decomposition of the oxide was carried out in an apparatus consisting essentially of a glass tube containing an iron spiral fixed at its extremities to two platinum bands passing through the tube; the tube is furnished with two small side-tubes fitted with perfectly air-tight taps.

Before the experiment the tube with the iron spiral was completely exhausted of air and weighed empty.

The analysis of the nitrous oxide consisted in causing the N_2O gas, set free from the tube with charcoal, to pass very slowly over the iron spiral, raised to incandescence (red-hot) by the electric current.

At the end of the experiment, having shut off the charcoal tube, a vacuum was made in the spiral tube by connecting the lower delivery tube to the mercury pump and continuing to heat the iron spiral, in order to prevent the fixation of nitrogen as nitride of iron.

All the weighings were carried out with counter-weights of the same glass and of practically the same volume.

For the details, I refer you to the complete memoir, only transcribing here our results.

TABLE XIII.—Atomic Weight of Nitrogen from the Gravimetric Analysis of Nitrous Oxide.

Nitrous oxide.	Oxygen.	Atomic weight N.
1.1670	0.4242	14.009
0.9498	0.3453	14.005
0.8652	0.3145	14.008
1.2247	0.4455	13.992
1.4202	0.5159	14.007
Mean		14.007

The mean weight of oxygen weighed being 0.4 gm., corresponding to 1.1 gm. of suboxide, the gravimetric errors are, if added, $\frac{1}{4000} + \frac{1}{10000} = \frac{3.4}{10000}$, and if they

compensate one another $\frac{1.6}{10000}$, giving a mean of $\frac{2.5}{10000}$.

The possible error ΔN resulting on the atomic weight of nitrogen will therefore be approximately:—

$$N = \pm \frac{44}{2} \cdot \frac{2.5}{10000} = \pm 0.0055.$$

The conduct of these experiments is very delicate. We have had many failures, also Bogdan and I have sought to give this method of analysis a more precise form. After several attempts, we believe we have found a more perfect method than the former. It consists in arranging an iron spiral, heated electrically, in a glass receiver furnished with a single ground-glass stopper; this apparatus is

* From the *Bulletin de la Société Chimique de Paris*, 1905.

weighed, first exhausted of air, then filled with nitrous oxide; the spiral is then raised to incandescence, allowed to cool, again exhausted, and weighed a third time.

With a trial apparatus of small dimensions containing only 0.4 gram. of nitrous oxide, the following figures were obtained:—

N.
1.4'00
1.4'03
1.3'95

Mean . . . 1.4'004

The possible error on the atomic weight of nitrogen resulting from the uncertainty of the weight of the oxygen (about 0.1450 gram.) and of the corresponding nitrous oxide is—

$$\Delta N = \pm 0.015.$$

Until we get nearer to the desired limit of accuracy (one unit in the second decimal place of the atomic weight of nitrogen), no conclusion can for the moment be deduced from this preliminary result.

These experiments should be resumed with apparatus of greater dimensions, the construction of which has so far presented very great difficulties.

(To be continued).

THE PHYSICAL AND CHEMICAL PROPERTIES OF IRON CARBONYL.*

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S.,
Jacksonian Professor in the University of Cambridge,

and

HUMPHREY OWEN JONES, M.A., D.Sc., Fellow of Clare College, and Jacksonian Demonstrator in the University of Cambridge.

(Continued from p. 3).

Vapour Density and Dissociation.—Two vapour density determinations were made by Mond and Langer (*loc. cit.*) by V. Meyer's method in an atmosphere of hydrogen at the temperature of boiling xylene. The results were 93.8 and 92.4, the theoretical value is 98, so that slight dissociation is indicated.

A number of trial experiments showed that iron carbonyl vapour dissociated quietly without explosion when heated to a high temperature alone or in an inert gas.

A series of vapour density determinations were made by V. Meyer's method in various gases at different temperatures in order to show the effect of temperature, of admixture with inert gas or carbon monoxide, and of the rate of diffusion on the dissociation of iron carbonyl. Owing, however, to the great stability of the iron compound and its slow rate of dissociation, these effects are not so clearly seen as in the case of nickel carbonyl. In fact, so slowly does iron carbonyl dissociate, that accurate determinations can only be obtained at the lowest temperatures where no dissociation occurs and at the highest temperatures where complete dissociation is rapid; at the intermediate temperatures the dissociation is so slow that diffusion to the cooler parts of the tube takes place and the end-point of the evolution of gas is extremely uncertain.

Several series of determination of the vapour density were also made by Hofmann's method to show the effect of pressure and temperature on the dissociation of iron carbonyl; but again, owing to the slow rate of dissociation, the experiments had to be prolonged for an inconveniently long time before even an approximately constant volume was obtained. In these experiments it is advisable to protect the vapour as far as possible from light, since the decomposition of the iron carbonyl by light, which takes place at low temperatures, is thus minimised.

The results obtained are tabulated below. The percentage dissociation is calculated by means of the formula—

$$p = \frac{D-d}{4d} 100.$$

Vapour Densities determined by Meyer's Method.

Temperature of the bulb.	Gas filling the tube.	Vapour density (H=1).	Percentage of Fe(CO) ₅ dissociated.
129° C. (amyl alcohol)	Carbon monoxide	93.7 } 93.2 }	1.2 (a)
	Nitrogen	90.1	2.2
	Hydrogen	86.2 } 88.7 } 87.5 }	3.0 (b)
155° C. (turpentine)	Carbon monoxide	82.6 } 78.0 }	4.6 6.4
	Nitrogen	36.4	42.3
182° C. (aniline)	Carbon monoxide	44.9 } 44.0 }	30.1
	Nitrogen	27.4	64.4 (c)
216° C. (naphthalene)	Carbon monoxide	20.2	96.3
	Nitrogen	20.0	97.5

Vapour Densities by Hofmann's Method.

Temperature.	Pressure.	Vapour density (H=1)g.	Percentage of Fe(CO) dissociated.
78° C.	195 195 212 288	99.8 98.4 100.0 99.8	— — — —
100° C.	126 179 204 225 298	98.3 98.6 97.2 97.1 99.5	— — — — —
130° C.	136 192 216 242 325	95.0 95.7 96.2 94.5 95.0	0.8 0.6 0.5 0.9 0.8
141 C.	261	86.6	3.3
155—160 C.	274 354	70.2 88.1	9.9 2.81
179° C.	249 334 406 574	40.4 } 40.4 } 44.2 } 45.6 }	35.6 (c) 30.2 28.8

Remarks.

- No visible deposit of iron.
- Distinct deposit of iron.
- Extensive deposit extending over large area of tube.
- Extremely faint deposit of iron.
- Very extensive deposit of iron; on cooling much undecomposed iron carbonyl condensed.

These results show very clearly the effect of increase of temperature and of diminution of pressure in increasing the dissociation, the effect of carbon monoxide in diminishing the dissociation observed in an inert gas at the same temperature. The increased dissociation in a light inert gas as compared with a heavy one is shown by the values in hydrogen and nitrogen at 129° C.

The rate of dissociation of the vapour at various temperatures was also studied in an apparatus very similar to that used by Mittasch for the dissociation of nickel carbonyl (*Zeit. Phys. Chem.*, 1902, vol. xl., p. 1). Owing to the small vapour pressure of iron carbonyl the range of pressures of undissociated vapour is very limited.

The rate of dissociation is very slow at temperatures below 180° C., but appears to be complete at that temperature. The reaction is reversible, but the reversal takes place very slowly.

* A Paper read before the Royal Society, November 16, 1905.

Chemical Reactions of Iron Pentacarbonyl.—An examination of some of the simpler reactions of iron carbonyl was made in order to study its chemical nature and stability in comparison with nickel carbonyl, the reactions of which have already been described (*Trans. Chem. Soc.*, 1904, vol. lxxxv, pp. 203—222). The action of the halogens in solution in pure dry carbon tetrachloride on normal and decinormal solutions of iron carbonyl in the same solvent was first investigated. The solutions were mixed in a nitrometer and allowed to stand, the gas evolved measured and tested, and the solid examined.

Chlorine and iron carbonyl react fairly rapidly to produce a solid and carbon monoxide, which was measured and showed that the decomposition was complete. The solid was found to be a mixture of ferrous and ferric chlorides. The ferrous chloride could never be obtained quite free from ferric, but by using a large excess of chlorine practically pure ferric chloride could be obtained. The gas appeared to be practically pure carbon monoxide and to contain no carbonyl chloride.

Bromine reacts with iron carbonyl very slowly—in fact, much more slowly than iodine reacts with nickel carbonyl. Five c.c. of a decinormal solution of iron carbonyl and 1 c.c. of normal bromine solution should evolve 22.4 c.c. of gas: 15 c.c. of gas had been evolved in six hours, 19.5 c.c. in 20 hours, and the reaction was practically complete in 35 hours. The solid salt consisted chiefly of ferrous bromide with minute traces of ferric salt; the gas was pure carbon monoxide. This reaction shows the much greater stability of the iron compound over the nickel compound, which is decomposed by bromine in a few seconds after mixing.

Iodine reacts extremely slowly with iron carbonyl to produce carbon monoxide and ferrous iodide; in decinormal solution the reaction had only proceeded to the extent of 70 per cent in three days.

Iodine monochloride in chloroform solution reacts with iron carbonyl much in the same way as it does with nickel carbonyl; ferrous chloride is precipitated and iodine liberated, the solution becoming purple; the free iodine then reacts very slowly with the residual iron carbonyl.

The whole reaction is a very slow one, and the salt at first precipitated is ferrous chloride, with no trace of ferric salt and no iodide; a little iodide appears before the formation of chloride is complete, but no ferric salt is produced.

Iodine trichloride in chloroform solution reacts slowly with iron carbonyl, producing a solid deposit and evolving gas; no free iodine is produced for a long time. The solid is again ferrous chloride free from ferric chloride, and contains very little iodide until the reaction has been proceeding for some time.

Cyanogen gas does not appear to react at all with iron carbonyl liquid or vapour, and in alcohol solution the reaction is extremely slow.

Cyanogen iodide in chloroform solution reacts very gradually, the solution first becoming red and then purple, and a brown solid is deposited. The solvent contains free iodine and the solid is ferrous cyanide mixed with a little ferrous iodide.

The action of the halogen hydrides was examined in the gaseous state and also in chloroform solutions.

Hydrochloric and hydrobromic acid gases had no action on iron carbonyl, even after allowing the mixture to stand for weeks in the dark. Dry **hydriodic acid** gas was introduced into an exhausted glass bulb containing a small glass bulb full of iron carbonyl which was then broken. On standing, a dark brown crystalline solid was produced, which was found to be ferrous iodide, and at the same time carbon monoxide and hydrogen were liberated.

In chloroform solution hydrochloric acid and hydrobromic acid react slowly with iron carbonyl, the former more slowly than the latter. In each case pure ferrous salts were produced and hydrogen and carbon monoxide were evolved. With a chloroform solution of hydriodic acid the reaction was more rapid and was complicated, as in the case of nickel carbonyl, by the liberation of iodine.

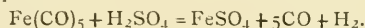
The reactions of iron carbonyl described above are exactly parallel with the corresponding reactions of nickel carbonyl, only differing in rapidity, which is much less owing to the greater stability of the iron compound. There is a more marked difference to be observed in some of the other reactions.

With **sulphur** dissolved to carbon bisulphide or xylene, iron carbonyl does not react at all in the cold, neither does it react with **nitric oxide**, in both cases differing markedly from nickel carbonyl.

Hydrogen sulphide also has no action on iron carbonyl, but an alcohol solution of the gas reacts extremely slowly to produce ferrous sulphide, carbon monoxide, and hydrogen.

Nitric acid in carbon tetrachloride or ether solution reacts rapidly with iron carbonyl to produce a mixture of ferrous and ferric nitrates, carbon monoxide with some hydrogen and reduction products of nitric acid.

Concentrated sulphuric acid reacts rapidly with iron carbonyl—the mixture first darkens, carbon monoxide and hydrogen are evolved, mixed with a little iron carbonyl vapour; the liquid then becomes paler in colour as the reaction is completed. The salt formed is pure ferrous sulphate, so that the reaction may be expressed by the following equation:—



The rapidity of the reaction is very much greater than in the case of nickel carbonyl; this is the only reaction yet observed which is more rapid than the corresponding reaction with nickel carbonyl.

To complete the comparison between the nickel and iron compounds in so far as the reactions of nickel carbonyl have been described, the reaction of iron carbonyl with **benzene** in presence of **aluminium chloride** was examined. Four grms. of iron carbonyl and 10 grms. benzene (five molecules) were poured on to 28 grms. powdered aluminium chloride (five molecules) in a tube, which was then sealed off and heated for two hours to 100° C. The mixture became very dark in colour, and on opening the tube some pressure caused by carbon monoxide and a little hydrochloric acid gas was observed.

The dark mass was mixed with ice, when some ferrous chloride dissolved and some ferrous hydroxide was precipitated, treated with hydrochloric acid and distilled in steam. Benzaldehyde and benzene came over first, followed by a crystalline fluorescent solid; the residue in the flask was dissolved in benzene, dried, and distilled, when a crystalline solid was obtained which was found to be pure anthracene, so also was the small quantity of solid which distilled in steam.

The final products of the reaction in this case are, therefore, precisely the same (namely, benzaldehyde and anthracene) as those produced by using nickel carbonyl. In the cold the reaction proceeds slowly, with the production of benzaldehyde and no anthracene, again precisely as in the case of nickel carbonyl.

(To be continued.)

Royal Institution.—On Tuesday next, January 16, at 5 o'clock, Professor E. H. Parker will deliver the first of a course of three lectures at the Royal Institution on "Impressions of Travel in China and the Far East"; on Thursday, January 18, at the same hour, Canon Beeching commences a course of two lectures on "Shakespeare"; on Saturday, January 20, at 3 o'clock, Mr. J. E. C. Bodley delivers the first of two lectures on "The Church in France." The Friday Evening Discourse on January 19 will be delivered by Professor J. J. Thomson, the subject being "Some Applications of the Theory of Electric Discharge to Spectroscopy"; on January 26 the discourse will be delivered by Mr. A. C. Benson, on "Walter Pater"; and on February 2 by Professor S. P. Thompson, on "The Electric Production of Nitrates from the Atmosphere."

THE CHEMICAL SEPARATION
OF THE RADIO-ACTIVE TYPES OF MATTER
IN THORIUM COMPOUNDS.*

By HERMAN SCHLUNDT and RICHARD B. MOORE.

(Continued from p. 9).

Separation by means of Fumaric Acid.

IN the course of our qualitative experiments several of the methods recently worked out for the quantitative separation of thorium from some of the other rare earth metals were tried. In this connection we found the contributions from the quantitative laboratory of Columbia University on the separation of thorium from cerium, lanthanum, and didymium very suggestive and helpful (Metzger, *Journ. Am. Chem. Soc.*, 1902, xxiv., 901; Neish, *Ibid.*, 1904, xxvi., 780).† The separation of thorium from the other metals named, by means of fumaric acid, as worked out by Metzger, when carried out with thorium compounds alone, effects a separation of some of the radio-active components. This fact was first noticed by Baskerville, who did not, however, identify the products (*Journ. Am. Chem. Soc.*, 1904, xxvi., 931). Metzger found that thorium is precipitated quantitatively from a neutral 40 per cent alcoholic solution by means of fumaric acid, while cerium, lanthanum, and didymium remain in solution. When thorium was precipitated by means of fumaric acid from a solution of thorium nitrate, ThX was found in the filtrate, together with some of the matter causing imparted activity. The precipitates and residues obtained were treated in the same manner as the products of the pyridine separation. The ThX was completely removed by two successive precipitations. The second precipitation was carried out by re-dissolving the first precipitate in hot dilute nitric acid, evaporating to dryness at 150°, re-dissolving in hot 40 per cent alcohol, and re-precipitating with fumaric acid. The activity of the residue obtained from the second filtrate was extremely small when compared with that of the residue obtained from the first filtrate, and it was found that one precipitation was sufficient to obtain the results presented below, provided the precipitate was thoroughly washed with hot 40 per cent alcohol containing a little fumaric acid. The activity of the residue obtained by evaporating the filtrate and igniting, to decompose the excess of fumaric acid, was found to exceed that obtained from the same amount of thorium nitrate, when the separation was carried out by means of pyridine, while the activity of the precipitate was correspondingly less. This difference was found to be due to the presence in the filtrate from the fumaric acid precipitate of a greater amount of the matter causing imparted activity. That a portion of this matter which causes the imparted activity had been separated from the thorium was shown in the following manner:—A sample of thorium nitrate, after undergoing three successive precipitations without lapse of time, with ammonia, when precipitated a fourth time with fumaric acid and the filtrate evaporated and ignited, yielded a minute residue of considerable activity. The residue was much more active than that obtained when the fourth precipitation was made with pyridine instead of with fumaric acid. The same amount of thorium nitrate was used in the two cases, and the time required for the experiments was approximately the same. During the first few hours after precipitation the activity of the residue increased in value, reaching a maximum in about four hours, when it decreased according to an exponential law, falling to half value in eleven hours. The Curve D, Plate I., which shows the change of activity with the time, has the form characteristic for the radio-active type of matter deposited on a negatively-charged plate

when exposed for a short time—about fifteen minutes—to the emanation of thorium oxide. The type of matter causing imparted activity was also separated from thorium compounds by first precipitating the thorium from the solution by means of fumaric acid, filtering, and then adding dilute ammonium hydroxide in excess to the filtrate, to which a drop of lead nitrate or ferric chloride solution had been added previous to the addition of ammonia. The small precipitate obtained contained the matter causing imparted activity which decays to half value in eleven hours, after passing through a maximum at approximately four hours from the time of precipitation. (Curve D, Plate I.)

Curves of Recovery and Decay.

The changes in radio-activity of the types of matter separated from thorium compounds by the foregoing methods are represented graphically in Plates I. and II. Curves *a*, *b*, and *c*, Plate I., represent the recovery of activity of the precipitates with the time, when the separations are carried out respectively with ammonia, pyridine, and fumaric acid. Curves *A*, *B*, and *C* show the decay of activity of the radio-active products obtained by evaporating the filtrates corresponding to the respective precipitates. In Plate II. the initial portions of the curves of decay and recovery are plotted on a larger scale, but the letters refer to the same products as in Plate I. Curve D, Plate I., shows the decay of activity of the matter causing imparted activity, which was removed by the two methods described above in connection with the fumaric acid separation. The curves represent, in the case of ammonia, three precipitations, with pyridine two, and with fumaric acid one.

In plotting the results the plan of Rutherford and Soddy (*Journ. Chem. Soc.*, 1902, lxxxi., 839) was followed. The activities are represented on the axis of ordinates by an arbitrary scale. In Plate I. the final value of the precipitates* was taken as 100 in each case. The recovery curves *a*, *b*, and *c* were plotted on this basis. In plotting the curves *A*, *B*, *C*, showing the decay in activity of the residues, the initial value is represented by 100, time being reckoned from the time the precipitation was made. In the case of Curve D, Plate I., the maximum value of the activity was placed at 100, and the time scale represents hours instead of days. Curves *A*, *B*, *C*, *a*, *b*, *c*, Plate II., are plotted on the basis of the initial values of the activities, both the precipitates and residues being taken as 100.

Neglecting for the present the initial irregularities of the curves of decay and recovery in Plate I.—a full discussion of which is given further on—it appears from the close parallelism of the curves after the second day that the same radio-active process is taking place in each set of residues and precipitates. After the second day the three residues have approximately the same activity. The same is true of the precipitates. The activity of the residues decays according to an exponential law, falling to half value in about four days—a rate of decay characteristic of ThX. In each separation the initial activities of the precipitates are about the same, values varying from 41 to 46 having been obtained in different experiments. These precipitates recover their activity in a geometric progression with the time, attaining a maximum value within a month, which is due to the formation of ThX and its disintegration products. When the recovery curves are extended back they cut the axis of ordinates at about twenty, which represents the proportion of the final activity due to the “non-separable” activity of thorium, which as Rutherford and Soddy have pointed out, may be regarded as a distinct type of matter resulting from the slow disintegration of the inactive thorium itself, and very closely allied to thorium in its properties, or it may be regarded as the radio-activity due to thorium itself. The value of the non-separable activity found by us is somewhat less than that given by Rutherford and Soddy, viz., 25 per cent; but in this connection it must be noted that these investigators record a value of

* From the *Journal of Physical Chemistry*, ix., No. 8, p. 682.† The contributions from the Harrison Laboratory, University of Pennsylvania, on the use of organic bases in precipitating and separating the rare earth metals likewise indicated other methods. (See *Journ. Am. Chem. Soc.*, 1902, xxiv., 540; 1903, xxv., 421, 1128).

* The effect due to the emanation is not included in the values.

22 per cent for the non-separable portion in one of their experiments. Inactive thorium was not obtained in the course of the separations. Hoffmann and Zerban (*Ber.*, 1903, xxxvi., 3093) and Zerban (*Ibid.*, 1903, xxxvi., 3911; see also Baskerville and Zerban, *Journ. Am. Chem. Soc.*, 1904, xxvi., 1642), state that inactive thorium was obtained from the mineral gadolinite. On the basis of the non-activity of thorium the activity of thorium compounds must be ascribed to a radio-active type of matter generally associated with thorium and very like it in its behaviour towards different reagents. If this view should prove to be the correct one, then—as Rutherford and Soddy have pointed out—the rôle played by the non-separable activity in the theory of radio-active changes would simply have to be assigned to the new radio-active matter so closely resembling thorium in its other properties.

Coming now to the consideration of the initial irregularities in the curves of decay and recovery, it is seen that the residues obtained from the filtrates in the fumaric acid and pyridine separations increase in activity considerably more than the ammonia residue. Moreover, the fumaric acid and pyridine residues attain their maximum after five hours, while the ammonia residue only reaches a maximum after nearly twenty hours. On the other hand, the precipitates obtained with fumaric acid and pyridine drop in activity more rapidly at first than the ammonia precipitate, the curves passing through minimum values at the same time that the curves of decay of the corresponding residues attain maximum values. These differences in the curves are more evident from the plotting in Plate II., which shows simply the initial portions of the curves.

The maximum and minimum in the curves of decay and recovery have been satisfactorily explained by Rutherford and Soddy when the separation is carried out by means of ammonia. Their explanation is briefly as follows (Rutherford, "Radio-activity," pp. 295–299; Soddy, "Radio-activity," pp. 117–121):—Before any separation is made the activity observed is the sum of the several activities of (1) thorium, (2) ThX, (3) emanation, (4) matter causing imparted activity, the last named consisting of at least two stages recently designated by Miss Slater as ThA and ThB respectively (*Phil. Mag.* [6], ix., 628, May, 1905). The separation with ammonia yields a precipitate free from ThX and without emanating power at first. In the precipitate is found the thorium and the matter causing imparted activity (both stages). Immediately after the separation then neither the residue from the filtrate nor the precipitate is in radio-active equilibrium. Since the precipitate is free from ThX, which produces the matter causing imparted activity, via the emanation, but little imparted activity will be produced during the first day, because comparatively little ThX is present. In view of the very rapid change of the emanation into the matter causing imparted activity—one-half changing in about one minute—no serious error is introduced by omitting this step in an explanation of the initial irregularities of the curves. The imparted activity present in the precipitate, however, decays, and since its rate of decay is *faster* than the rate at which ThX is formed, the activity of the precipitate decreases for a time until the activity of the ThX and its disintegration products compensate the loss of activity due to the decay in the matter causing imparted activity. Rutherford and Soddy established the correctness of this view by separating ThX from thorium twenty-three times during a period of nine days, so as to remove the ThX nearly as fast as it was formed, while at the same time the matter causing imparted activity decayed. The recovery curve then obtained showed practically no drop, and finally after about a month attained a constant value approximately four times its initial value.

The initial rise in the ThX curve is explained by considerations similar to those advanced for the decay in activity of the precipitate during the first day. ThX changes into the matter causing imparted activity, and as the latter disintegrates more rapidly than ThX, the activity due to the imparted activity more than com-

pensates for the decay in activity of ThX itself; and the combined effect of these two activities gradually increases during the first day after precipitation, the maximum lying about 18 per cent higher than the initial value. The theoretical curve showing the combined effect of two radio-active types of matter, the first producing the second, and having respectively the radio-active constants of ThX and the imparted activity considered by them, is given by Rutherford on p. 299 of his book on "Radio-activity" (see also Curve A, Plate I.). The observed and theoretical values show a very good agreement.

(To be continued).

THE VOLUMETRIC ESTIMATION OF CYANATES.*

By A. C. CUMMING, B.Sc., and ORME MASSON, F.R.S.

(Concluded from p. 6).

As it was impossible to obtain perfectly pure cyanide or cyanate from which to make up mixtures of known composition, we decided to test the method by applying it first to separate stock solutions (a) of cyanide containing traces of carbonate and cyanate, and (b) of cyanate containing a trace of cyanide and a fair amount of carbonate, and then to apply it to mixtures of these in different proportions. If the method is trustworthy, the results obtained with the mixtures should agree with those calculated from the first analyses of the stock solutions; but there should be no such agreement if any or all of the analyses are incorrect. It seemed useless to attempt to check the results by independent analytical methods, as we know of none that can be regarded as wholly satisfactory.

In the first place stock solutions were made of approximately 0.1 N. KCN and 0.066 N. KCNO. Two mixtures of these were made, one (A) containing equal volumes, the second (B) containing 4 volumes of the former to 1 of the latter. The results were as follows:—

Cyanide Solution.					
	I.	II.	III.	Mean.	
CN	0.0986	0.0984		0.0985	
$\frac{1}{2}$ CO ₃	0.0020	0.0017		0.0019	
CNO	0.0018	0.0003		0.0010	
Cyanate Solution.					
CN	0.0019	0.0019	—	0.0019	
$\frac{1}{2}$ CO ₃	0.0256	0.0246	0.0246	0.0249	
CNO	0.0648	0.0663	0.0663	0.0658	
Mixture A.					
	I.	II.	III.	Mean.	
CN	0.0499	0.0499	—	0.0499	0.0502
$\frac{1}{2}$ CO ₃	0.0141	0.0146	0.0139	0.0142	0.0134
CNO	0.0329	0.0323	0.0334	0.0329	0.0334
Mixture B.					
CN	0.0777	0.0779	—	0.0778	0.0792
$\frac{1}{2}$ CO ₃	0.0065	0.0068	0.0063	0.0065	0.0065
CNO	0.0161	0.0143	0.0142	0.0149	0.0140

Free alkali present, if any, was included in the figures given for carbonate. The cyanide was titrated with silver nitrate in the usual way, and the total alkali and the cyanate were determined by titration with congo indicator, as described in the previous part of this paper.

To ascertain whether the method would work in the case of stronger solutions, some of about ten times the former strength were made up and tested before and after mixing. The results were as follows:—

* Communicated by the Authors. From the *Proceedings of the Society of Chemical Industry of Victoria*, July–August, 1903.

Cyanide Solution.

	I.	II.	III.	Mean.
CN	0.978	0.978	—	0.978
$\frac{1}{2}$ CO ₃	0.026	0.032	0.032	0.030
CNO	0.013	0.015	—	0.014

Cyanate Solution.

	I.	II.	III.	IV.	V.	VI.	Mean.
CN	0.005	0.005	—	—	—	—	0.005
$\frac{1}{2}$ CO ₃	0.083	0.082	0.082	—	—	—	0.082
CNO	0.030	0.019	0.032	0.052	0.038	0.034	0.034

Mixture (Ten vols. Cyanide to One vol. Cyanate).

	I.	II.	Mean.	
			Found.	Calculated.
CN	0.890	0.890	0.890	0.889
$\frac{1}{2}$ CO ₃	0.037	0.037	0.037	0.035
CNO	0.073	0.073	0.073	0.070

These results seem to justify the recommendation of the method for the analysis of commercial samples of potassium or sodium cyanide. Certain precautions are, however, necessary.

In the first place, grave errors may be introduced in the calculation of the carbonate from the total alkali by subtraction of the cyanide, unless the acid used is reduced to the same true standard as the silver nitrate. Any small difference that may exist is thrown upon the carbonate. We prefer to use HCl standardised with Iceland spar and AgNO₃ standardised with the CaCl₂ solution obtained in the same operation (Masson, CHEMICAL NEWS, lxxxi., 73).

In the second place, the presence of much cyanate undoubtedly introduces some difficulty in the judging of the end-point in the cold titration with acid for total alkali. The best results are obtained by considerably diluting the solution, and running in the standard acid very slowly and with frequent agitation. This prevents local decomposition of cyanate by excess of acid before the true end-point is reached. Another obvious advantage of large dilution is that the evolution of HCN is less troublesome. We have made a few tests to compare the results obtained for carbonate as above with those got by the method first recommended (we believe) by Mellor, viz., the titration with acid of the faintly-clouded solution of KAg(CN)₂ obtained in the cyanide titration. This method, using congo as indicator, gives a very sharp end-point. The results seem to be slightly lower than those got by direct alkalimetry of the KCN solution, but we cannot say definitely that they are more accurate.

Thirdly, impure commercial cyanides may of course contain various substances which would tend to spoil the carbonate and cyanate determinations. As an instance, we find that much ferrocyanide is fatal, though traces do not seem to have any notable influence. But at the present day commercial cyanide is, as a rule, of high quality.

The cyanate values in the preceding tables were all obtained by the back titration after boiling with excess of acid, and not by the loss of NH₃, which results later in the carrying out of the full method as previously described (*loc. cit.*). This check was, however, employed in one case—that of the strong cyanide solution—which gave the CNO as 0.014 and 0.015 N. as against the 0.013 and 0.015 already quoted.

It is obvious from the above results that the two determinations give equal results if NH₄ salts be not present in the original sample. But still it seems doubtful whether this would be the case if the HCN were not quickly got rid of in the first boiling with excess of acid, as it is probable that prolonged treatment of this sort would hydrolyse some of the cyanide with production of NH₃. As some of the analytical methods that have been recommended by others would be spoilt by such an action, it appeared worth while to test the question. For this purpose the same quantity of the same normal cyanide solution as was used previously was boiled for about three hours with excess of sulphuric

acid in a flask provided with a reflux condenser, and the ammonia was then determined. The quantity obtained, if assumed due only to the decomposition of cyanate, would make the latter 0.030 N., whereas the true value was 0.014 N., as already shown. It seems, therefore, that there is some danger in such prolonged heating, though it is certainly negligible when the boiling is effected quickly in an open vessel, as is our practice.

University of Melbourne.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 21st, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MESSRS. P. W. Robertson, Arthur Slator, J. I. Scott, and E. Townyn Jones were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Thos. Going Stoney Bogue, 5, Kenilworth Square, Dublin; Stephen Lewis Courtauld, B.A., Bocking Place, Braintree; Henry Carlyle Irving, B.A., 14, Heath Hurst Road, Hampstead. N.W.; John McDowall, Girdstingwood, Kirkcudbright, Scotland; John Parkin, M.A., Blaithewaite, Carlisle; William Hughes Perkins, B.Sc., Harpur Hill, near Buxton; Philip Foale Rowsell, Nutbrook, Exmouth; John William Yates, B.Sc., 71, North Street, Hugglescote, near Leicester.

A certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Hardolph Wastenays, of Brisbane, Queensland.

Of the following papers, those marked * were read:—

*218. "*Azo-derivatives from Methyl-a-naphthocoumarin.*" By JOHN THEODORE HEWITT and HERBERT VICTOR MITCHELL.

The methyl-a-naphthocoumarin, obtained by the condensation of a-naphthol and ethyl acetoacetate, when dissolved in hot caustic alkalis, yields alkali coumarinates, and if these solutions are cooled and treated with the solution of a diazonium salt, coupling takes place in the usual manner. On acidifying the solution, the corresponding azocoumarin is precipitated, and in none of the four cases examined has the formation of an azocoumarinic acid been observed.

The following substances have been prepared:—*Benzene-azomethylnaphthocoumarin* (m. p. 207°); *o-nitrobenzene-azomethylnaphthocoumarin* (m. p. 268°); *m-nitrobenzene-azomethylnaphthocoumarin* (m. p. 239°); *p-nitrobenzene-azomethylnaphthocoumarin* (m. p. 270–271°). The last of these compounds is remarkable in giving an intense blue coloration in alkaline solution, the alkaline salts derived from the other compounds being orange or red in aqueous solution.

*219. "*The Preparation and Reactions of Benzoyl Nitrate.*" By FRANCIS ERNEST FRANCIS.

Lachowicz showed (*Ber.*, 1884, xvii., 1281) that when benzoyl chloride or other chlorides of the mono- and dibasic organic acids interact with silver or other metallic nitrates, decomposition into oxides of nitrogen and the corresponding organic anhydrides takes place.

If, however, the interaction of benzoyl chloride with silver nitrate is effected at much lower temperatures, oxides of nitrogen are not evolved, and benzoyl nitrate is formed, $C_6H_5 \cdot COCl + Ag \cdot O \cdot NO_2 = C_6H_5 \cdot CO \cdot O \cdot NO_2 + AgCl$.

The product is a light yellow oil which, if carefully warmed, decomposes quantitatively into benzoic anhydride and oxides of nitrogen, but if heated with a free flame this change sets in with explosive violence, the yield of anhydride being much diminished.

Benzoyl nitrate is very rapidly attacked by moisture with

the formation of benzoic and nitric acids. When kept at low temperature either by itself or dissolved in an inert solvent, an interesting change into *m*-nitrobenzoic acid takes place without the formation of either the *o*- or *p*-acid.

Between 0° and -15° , ethyl alcohol and the nitrate give ethyl nitrate, benzene and toluene are converted into their mononitro-derivatives, and phenetole and phenol undergo nitration quantitatively, the product from the former being apparently *o*-nitrophenetole. Methylaniline is nearly quantitatively converted into phenylmethylnitramine, and in all these reactions benzoic acid is simultaneously formed. Aniline, however, gives aniline nitrate and benzanilide. From these observations, it seems probable that benzoyl nitrate will prove to be generally applicable in effecting nitration at low temperatures and in the absence of water.

*220. "The Supposed Identity of Dihydrolaurole and of Dihydroisolaurole with 1:1-Dimethylhexahydrobenzene." By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

The hydrocarbons dihydrolaurole and dihydroisolaurole have been prepared according to the directions given by Zelinsky and Lepeschkin (*Annalen*, 1901, cccxix., 303), and their properties carefully compared with those of 1:1-dimethylhexahydrobenzene (*Trans.*, 1905, lxxvii., 1488). The above-mentioned authors supposed that these three substances were one and the same, but this is not so, for neither dihydrolaurole nor dihydroisolaurole is identical with 1:1-dimethylhexahydrobenzene.

The constitution of dihydrolaurole is still doubtful, but dihydroisolaurole has been proved conclusively to be a pentamethylene derivative, and is 1:1:2-trimethylcyclopentane.

*221. "The Diazo-derivatives of 1:5- and 1:8-Benzene-sulphonylnaphthylenediamines." By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

The behaviour of the benzenesulphonyl derivatives of the 1:5- and 1:8-naphthylenediamines towards nitrous acid has been studied in order to ascertain whether these acylated heteronuclear diamines are capable of yielding diazoimides, and if so to compare the products with the reactive yellow arylsulphonylparadiazoides and the inert colourless acylorthodiazoides.

Benzenesulphonyl-1:8-naphthylenediamine (m. p. 166°) obtained by reducing benzenesulphonyl-8-nitro- α -naphthylamine (m. p. 194°), yields a soluble diazonium salt which, by the action of aqueous sodium acetate, gives rise to benzenesulphonyl-1:8-naphthylenediazoimide, $C_{10}H_6[N_3] \cdot SO_2 \cdot C_6H_5$; this product is a well-defined, crystalline, yellow diazoanhydride comparable in every respect with the paradiazoides already described by the authors.

This result indicates that the property of yielding these coloured diazoimides is not confined to the *p*-diamine series, and that the characteristic physical and chemical properties of the products do not necessarily arise from the possession of a paraquinonoid configuration.

as-Benzenesulphonyl-N-methyl-1:8-naphthylenediamine and benzenesulphonyl-1:5-naphthylenediamine furnish diazonium salts which are not appreciably affected by aqueous sodium acetate.

*222. "Further Experiments on a New Method of Determining Molecular Weights." By PHILIP BLACKMAN.

When working with solvents of high boiling-point, the operations (*Trans.*, 1905, lxxvii., 1474) must be carried out under reduced pressure, this reduction being effected by means of a filter-pump.

To prevent ejection of liquid or mixing, due to violent boiling, two bulbs, instead of one, should be introduced into each limb of the inverted U-piece.

Most of the vapours condense in the bulbs; when a considerable quantity has thus collected in the bulbs, the volumes of the solutions in the test-tubes are observed, care being taken that the liquid in the bulbs does not flow back into the test-tubes during the reading. The liquid is then

allowed to return into the tubes, the boiling is repeated, and a reading again taken. This process is repeated as often as is convenient.

A condenser should not be used. Instead of platinum wire, broken pieces of glass were employed. The method works best with volatile solvents, such as acetone (b. p. $56.5-57^{\circ}$), alcohol (96 per cent), and benzene (b. p. $80-82^{\circ}$).

*223. "Studies in Fermentation. The Chemical Dynamics of Alcoholic Fermentation by Yeast." By ARTHUR SLATOR.

The chief results obtained may be summarised as follows:—

1. In the study of the rate of alcoholic fermentation, many complications are eliminated by measuring the velocity over very small ranges of the reaction.

2. The change in pressure due to evolution of carbon dioxide is a convenient and sensitive method of measuring this velocity.

3. The rate of fermentation of dextrose is proportional to the concentration of yeast over a wide range of concentrations.

4. The rate is almost independent of the concentration of sugar except in very dilute solutions. The influence of this concentration is never so great that the velocity is proportional to the concentration of the sugar; the reaction is therefore never one of the first order with regard to the sugar.

5. The temperature-coefficient of the reaction is large, and varies with the temperature. $V_{15}/V_5 = 5.6$, $V_{40}/V_{30} = 1.6$, and intermediate values are obtained between these temperatures. The temperature quotient for 5° from 5° to 40° forms a series of numbers which seem to be characteristic of the enzyme zymase.

6. The initial rates of fermentation of dextrose, lævulose, sucrose, and maltose are in the ratio 1:0.92:1.05:0.9.

7. The temperature-coefficient of the reaction inhibited by "poisons" is the same as that of the original reaction.

8. It is improbable that any but small quantities of sugar go through the intermediate step of lactic acid in fermentation.

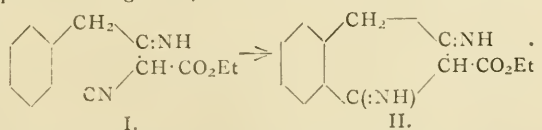
9. These results indicate that the reaction which is measured in these experiments is the slow decomposition of a compound produced by the interaction of the enzyme and the sugar.

*224. "Some New Platinocyanides." By LEONARD ANGELO LEVY and HENRY ARNOTT SISSON.

The authors described and gave the results of the analysis of hydrazine and hydroxylamine platinocyanides. These salts form unstable hydrates, which are easily produced by slight changes in temperature. The alteration in the state of hydration is accompanied by striking colour changes.

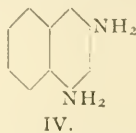
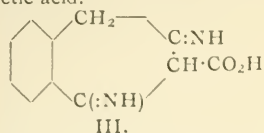
*225. "An Intramolecular Change Leading to the Formation of Naphthalene Derivatives." By ERNEST FRANCIS JOSEPH ATKINSON and JOCELYN FIELD THORPE.

Ethyl sodiocyanoacetate condenses with benzyl cyanide to form ethyl α -cyano- β -imino- γ -phenyl-*n*-butyrate, $Ph \cdot CH_2 \cdot C(:NH) \cdot CH(CN) \cdot CO_2Et$, a colourless substance crystallising from alcohol in large prisms melting at 125° ; its constitution is proved by the fact that on hydrolysis with alcoholic potash it yields phenylacetic and malonic acids. The new imino-ester (I), when treated with an equal weight of cold concentrated sulphuric acid, forms an intense green solution, which, when diluted with water and rendered alkaline with ammonia, gives ethyl 1:3-diamino-naphthalene-2-carboxylate (II), forming intense yellow prisms melting at 104° .



The hydrochloride forms colourless needles. Ethyl 1:3-diamino-naphthalene-2-carboxylate, on treatment with

methyl-alcoholic potash, gives a potassium salt from an aqueous solution of which 1 : 3-diaminonaphthalene-2-carboxylic acid (III.) is precipitated on acidifying with acetic acid.



The acid forms slightly coloured needles from warm water, which decomposes at about 85°, and when heated at this temperature until the evolution of carbon dioxide has ceased are transformed into 1 : 3-naphthlenediamine (IV.) which, when re-crystallised from dilute alcohol, forms small plates melting at 96°.

The diacetyl derivative forms needles from glacial acetic acid melting at 263°.

DISCUSSION.

In reply to questions from Drs. Forster and Morgan. Dr. THORPE said that the reaction with cold sulphuric acid proceeded very rapidly, and was complete after about one minute, the yield being practically quantitative. Hitherto the yield of ethyl α -cyano- β -imino- γ -phenyl- n -butyrate only amounted to 25 per cent, but by slightly altering the conditions of the experiment it was hoped that this amount would be largely increased. The temperature at which the condensation was carried out greatly influenced the quantity of the condensation product formed.

226. "The Relation of Position Isomerism to Optical Activity. V. The Rotation of the Menthyl Esters of the Isomeric Dibromobenzoic Acids." By JULIUS BEREND COHEN and ISRAEL HYMAN ZORTMAN.

In continuation of previous investigations on this subject (*Trans.*, 1903, lxxxiii., 1213; 1904, lxxxv., 1262, 1271; 1905, lxxxvii., 1190), the present communication contains an account of certain physical constants, including the molecular rotations of the six isomeric menthyl dibromobenzoates. With the exception of the 2 : 6-ester, the effect on the rotation of the substitution of two bromine atoms is generally less than that of two chlorine atoms, or one chlorine and one bromine, in the same positions. The magnitude of the deviation, beginning with the ester of smallest rotation, is 2 : 6; 2 : 3; 2 : 5; 2 : 4; 3 : 5; 3 : 4; phenyl. The order is the same as that of the dichloro- and chlorobromobenzoates with the exception of the 3 : 4- and 3 : 5-esters, the positions of which in the present case are reversed. The influence of the ortho-bromine atom in depressing the rotation is very clearly indicated in all cases, but most strikingly in that of the 2 : 6-ester, which shows a rotation of $[\text{M}]_D^{20} - 19.5^\circ$ compared with the next lowest (2 : 3), which gives $[\text{M}]_D^{20} - 173.2^\circ$, or with menthyl benzoate, in which $[\text{M}]_D^{20}$ is -236.3° .

227. "Some Derivatives of Naphthoylbenzoic Acid and of Naphthacenequinone." By JAN QUILLER ORCHARDSON and CHARLES WEIZMANN.

The authors have investigated a series of condensations which have resulted in the preparation of substitution derivatives of naphthoylbenzoic acid, and from these, by the action of concentrated sulphuric acid, they obtained the corresponding substituted naphthacenequinones.

228. "Ethyl β -Naphthoylacetate." By CHARLES WEIZMANN and ERNEST BASIL FALKNER.

β -Naphthoyl acid was converted into β -naphthoyl chloride, $\text{C}_{10}\text{H}_7\text{CO}\cdot\text{Cl}$, by treatment with phosphorus pentachloride, and this chloride was then allowed to react with the sodium derivative of ethyl acetoacetate. The ethyl β -naphthoylacetate, $\text{C}_{10}\text{H}_7\text{CO}\cdot\text{CH}_2\text{CO}\cdot\text{CH}_3$, melted at 57°, and when digested with ammonia and ammonium chloride yielded ethyl β -naphthoylacetate, which melted at 34°, and gave rise to a hydrazone (m. p. 95°).

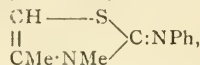
229. "Contributions to the Chemistry of the Amidines. 2-Aminothiazoles and 2-Imino-2 : 3-dihydrothiazoles. 2-

Iminotetrazithiazoles and 2-Amino-4 : 5-dihydrothiazoles." By GEORGE YOUNG and SAMUEL IRWIN CROOKES.

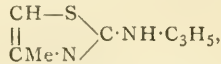
It was shown that the alkylation of amidines belonging to the thiazole group which have one of the nitrogen atoms and the carbon atom of the group —N:C:N— , forming part of a closed chain, whilst the other nitrogen atom lies outside the cyclic nucleus, leads to the formation of derivatives in which the alkyl group is attached to the nitrogen atom of the nucleus, except when the ring is already partially reduced and an aryl group is attached to the nitrogen atom of the side-chain, to which, in this case, the alkyl group becomes attached. Methylation of an amidine takes place by addition of methyl iodide and subsequent elimination of the hydrogen haloid.

The following substances were described :—

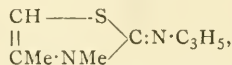
Acetyl-2-anilino-4-methylthiazole, $\text{C}_{10}\text{H}_9\text{N}_2\text{S}\cdot\text{Ac}$, forms clusters of soft, white needles (m. p. 114.5°); 2-phenylimino-3 : 4-dimethyl-2 : 3-dihydrothiazole,—



separates in small, white crystals (m. p. 65–66°), and forms a platinichloride (m. p. 189–190°). 2-Allylimino-4-methylthiazole,—

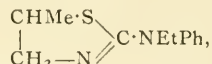


crystallises in long, white needles (m. p. 40–41°), and forms an acetyl derivative (m. p. 36–37°). 2-Allylimino-3 : 4-dimethyl-2 : 3-dihydrothiazole,—



is a slightly red, viscid oil which forms a hydriodide (m. p. 116–117°). The silver derivative of 2-acetylmino-4-methyl-2 : 3-dihydrothiazole yields, on methylation, 2-acetylmino-3 : 4-dimethyl-2 : 3-dihydrothiazole (m. p. 113°); 2-methylamino-4-methylthiazole (m. p. 64°) yields, on methylation, 2-methylmino-3 : 4-dimethyl-2 : 3-dihydrothiazole hydriodide (m. p. 164°).

2-Phenylimino-5-methyltetrahydrothiazole forms a silver derivative decomposing at 130° and an acetyl derivative melting at 47°; 2-phenyl-methylamino-5-methyl-4 : 5-dihydrothiazole picrate forms soft yellow needles (m. p. 114–115°); 2-phenylethylamino-5-methyl-4 : 5-dihydrothiazole,—



is oily, and forms a platinichloride decomposing at 156°.

A similar series of compounds, in which the β - and α -tolyl groups replace the phenyl group of the foregoing substances, has also been prepared.

When successively oxidised and hydrolysed, the 2-arylalkylamino-5-methyl-4 : 5-dihydrothiazoles yields β -methyltaurine, which melts at 284–285°, and the corresponding arylalkylamine.

230. "The Action of Water on Diazo-salts." By JOHN CANNELL CANE and GEORGE MARSHALL NORMAN.

The authors have extended the work already briefly described (*Proc.*, 1905, xxi., 206) to the examination of the diazo-salts from 2 : 4-dibromoaniline and dibromo- p -toluidine ($\text{CH}_3\text{:NH}_2\text{:Br:Br:1:4:3:5}$), and in each case were successful in obtaining the corresponding substituted phenols. The results of a series of researches carried out during the past four years by the author and his assistants have been summarised.

231. "Note on the Atomic Weight of Nitrogen." By ALEXANDER SCOTT.

By the titration of ammonium bromide against silver, the author (*Trans.*, 1901, lxxix., 154) obtained results which differed notably from those of Stas, although the

values from the chloride seemed to agree somewhat better. These values were:—

	Stas.	Scott.
NH ₄ Cl	= 53.532	53.516
N	= 14.045	14.029
NH ₄ Br	= 98.032	97.995
N	= 14.047	14.010

Stas' values for the atomic weight of nitrogen agree with one another, whilst those of the author do not. These values depend, however, on the correctness of the atomic weights taken for chlorine and for bromine, which were assumed to be 35.457 for chlorine and 79.955 for bromine.

By the recent determinations of T. W. Richards and R. C. Wells ("A Revision of the Atomic Weights of Sodium and Chlorine," 1905), published by the Carnegie Institution of Washington, the want of agreement in the author's values has been completely cleared up, and the discrepancy (to an equal extent) transferred to the determinations made by Stas. They prove that Cl = 35.473.

The work of the author was criticised last year by T. W. Richards (*Proc. Am. Phil. Soc.*, 1904, xliii., 116), who maintained that 14.01 was too low for the atomic weight of nitrogen, and at the end of his paper he states that:—"It seems probable that the atomic weight of nitrogen is not less than 14.02 and not over 14.04, probably being nearer to the latter value than to the former."

The physical work of Lord Rayleigh and of Leduc on this problem as well as the chemical and physical work of Guye and his co-workers, and of R. W. Gray (*Trans.*, 1905, lxxvii., 1601) all render the conclusions of Richards quite untenable. It is most interesting that the author's critic should, by his own work, have brought the values of the author, which are cited above, completely into line with those of other recent workers. Using 35.473 instead of 35.457 for the atomic weight of chlorine as above, the author's values for the atomic weight of nitrogen become 14.013 from the chloride and 14.010 from the bromide. When it is remembered that only one gravimetric and two volumetric determinations were made with the chloride, closer agreement could not be expected, and the value 14.010 deduced from the large number of experiments made with the bromide seems completely established.

With regard to the suggestion that the low value found by the author for the bromide was due to his hydrobromic acid containing chlorine, the results given in his paper on the preparation of pure hydrobromic acid (*Trans.*, 1900, lxvii., 651) are a sufficient answer. The bromine used was purified by the method given by Stas, by solution in potassium bromide with the addition of zinc oxide. It ought to have been stated that the silver used in Experiment VI.(b) (*Trans.*, 1901, lxxix., 152) was cleaned by acid, as recommended by Richards, after fusion on lime and before it was heated in hydrogen.

232. "The Solubility of Zinc Hydroxide in Alkalis."

By JAMES MOIR.

When the precipitate of zinc hydroxide dissolves in excess of caustic alkali, the phenomenon is essentially an equilibrium between the alkali and zincic acid, and this equilibrium may be reached from both sides:—(1) addition of excess of zinc hydroxide to caustic alkali, and (2) dilution with water of a strong solution previously saturated with zinc hydroxide. In the latter case, some of the hydroxide is re-precipitated and an equilibrium is slowly reached, which, as in the first case, depends solely on the concentration of the free alkali.

Observations have been made on both lines over the range from 7 N to 0.01 N alkali, below which the amount of zinc dissolved is insignificant, being little greater than that due to the solubility of zinc hydroxide in pure water. In addition, the author has succeeded in showing that the experimental results can be deduced from the ordinary assumptions of the ionic theory; so that it follows that the solubility of zinc hydroxide in alkali depends solely on the concentration of hydroxidion in the solution.

It is also shown that no definite chemical compounds (such as ZnO,8KOH) exist, since the curve obtained by

plotting the results is approximately a parabola, and its tangent never passes through the origin.

A practical result of the investigation is to show that in working cyanide solutions scarcely any of the zinc is present as zincate, but nearly all is zincocyanide.

The formula, giving the dissolved zinc in terms of the concentration of alkali, is $y = 0.004x \left(\frac{79x+6}{x+2} \right)$; where y and x are expressed in grm.-molecules.

The following list gives a comparison of calculated values of y with those obtained by interpolation from the experimental curves:—

	$x =$	y Calculated =	y Observed =
1. 7.5 N NaOH ..	7.5	1.89	1.692
2. 5.5 N KOH ..	5.5	1.291	1.36
3. 2.5 N NaOH ..	2.5	0.452	0.48
4. 2.0 N KOH ..	2.0	0.328	0.32
5. 1.5 N KOH ..	1.5	0.2033	0.21
6. 1.3 N NaOH ..	1.3	0.171	0.17
7. 1 N KOH ..	1	0.1132	0.110
8. 0.5 N NaOH ..	0.5	0.0364	0.040
9. 0.1 N NaOH ..	0.1	0.00265	0.0035
10. 0.05 N NaOH ..	0.05	0.00097	0.0010
11. 0.01 N NaOH ..	0.01	0.000135	0.0002

The theoretical results are usually a little too low, which points to a small error in the value of the constants assumed; but on the whole the agreement between theory and practice is as good as could be expected, considering that the experiments were not made at absolutely constant temperature. This agreement cannot be fortuitous, and vindicates the correctness of the assumptions made at the beginning regarding the constitution of zincate solutions and the applicability of the ionic theory. They show also that the whole phenomenon is not one of the formation of definite chemical compounds, but is purely conditioned by the strength of the alkali.

Some of the experimental results are abnormal, especially those obtained by diluting a strong saturated zincate solution. This effect is due to the persistence of the state of supersaturation. The reactions $K_2ZnO_2 + H_2O \rightarrow KHZnO_2 + KOH \rightarrow H_2ZnO_2 + 2KOH$ have evidently slow velocities, nevertheless the hydrolysis is eventually very complete, and ultimately the same result is obtained as if alkali of the final concentration had been treated with excess of zinc hydroxide. Zinc hydroxide, acting as zincic acid, has therefore a different constant of dissociation from its ordinary basic one, and, in fact, the constant of the equation $(H^+)(HZnO_2) = K \cdot (H_2ZnO_2)$ is rather less than that of water, a fact which accounts for the extensive hydrolysis of the salts of zincic acid.

233. "The Slow Combustion of Carbon Disulphide."

By NORMAN SMITH.

Experiments have been carried out in order to determine the composition of the reddish-brown deposit formed when carbon disulphide and oxygen are passed through a heated tube (compare Turpin, *Brit. Assoc. Reports*, 1890, 776; Dixon and Russell, *Trans.*, 1899, lxxv., 603). The deposit consists chiefly of an acidic compound C₁₆H₆O₄S₈. Another acidic substance or substances containing less carbon and more sulphur than the foregoing product, and very small quantities of free carbon and sulphur, are also found to be present. The silver and ammonium salts of the compound C₁₆H₆O₄S₈ have been prepared. The gaseous products consist chiefly of sulphur dioxide with small amounts of carbon dioxide.

An International Exhibition at Antwerp is announced for the months of April and May, 1906. Chemistry and Pharmacy will occupy very important places. Manufacturers are strongly advised to take part in this Exhibition, which is under Official patronage, and under the Honorary Presidentship of S. A. R. Madame la Comtesse de Flandres. Further particulars can be obtained from the Secretary, 26, Rue d'Arenberg, Antwerp (The Royal Artistic Club).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 24, December 11, 1905.

Distillation of Gold, of the Alloys of Gold with Copper and with Tin, and on a New Method of Preparation of Purple of Cassius.—Henri Moissan. *Distillation of Gold.*—Following the experience derived from the distillation of copper, the author by varying the time of action of a current of 500 ampères under 110 volts, acting on 150 grms. of pure gold, succeeded in distilling as much as 20 grms. of metal. He describes at length the residue of gold left in the crucible, which is found to be free from lime. The surface of the tube of copper, placed above the crucible and cooled by a current of water, is covered with a layer which, on examination with a lens, resembles that described in a previous note. Close to the tube were found very small yellow cubic crystals accompanied by a small quantity of lime and graphite. The vapour condensing on a bell-glass gave a beautiful purple deposit, consisting of a mixture of lime and distilled gold. The author then repeated these experiments in a carbon tube, the metal being placed in a graphite boat. Several small crystals of gold were found amongst a large number of metallic spherules, and the residue was covered by a film of graphite as above. The author concludes that the distillation of gold is more difficult than that of copper, and that it takes longer, and that gold is already volatile at the temperature of fusion of lime. The chemical properties of distilled gold are the same as those of hammered or molten metal reduced to a fine powder. Aqua regia and chlorine water attack it according to the degree of tenuity of the specimen. This is equally true for the action of fluorine or sulphuric acid and potassium permanganate. *Distillation of Alloys of Copper and Gold.*—Roberts-Austen has given the curve of fusibility of these alloys, and has shown that they form homogeneous solutions in all proportions up to a temperature of 1064°. The author has prepared an alloy containing 10 per cent of gold, and after heating 100 grms. for four minutes with a current of 500 ampères under 70 volts, obtained as residue 77 grms. Copper, 89.02; gold, 11.33 per cent. Another experiment with 39 grms. of 10 per cent gold gave, after five minutes,—Gold, 10.72; copper, 89.09. With a 50 per cent alloy he obtained:—(a) Gold, 50.22; copper, 49. (b) Gold, 57.02; copper, 42.81. He concludes that copper is certainly more volatile than gold. *Alloy of Gold and Tin.*—In this case numerous experiments show that tin distils more rapidly than gold, the actual figures being:—200 grms. of an alloy, containing 40 per cent of gold, heated for three minutes in a current of 500 ampères under 70 volts, left 185 grms. of residue, consisting of:—(a) Gold, 41.08; tin, 59.72; and for four minutes 149 grms. of residue—(b) Gold, 45.9; tin, 53.88. *Purple of Cassius.*—The purple powder obtained on the condensing tube and on the bell-glass is of the same colour as the areola round the little globule of gold condensed on the lime of the electric furnace some distance from the crucible, and due to the formation of anhydrous calcium oxide coloured by gold. It is, then, a new purple prepared by the volatilisation of gold, and the condensation of its vapour on the lime. When the vapour from the alloy of gold and tin is given off, the tin burns to oxide, and is mixed with the vapour of gold, which is unaffected by air; the substance formed has the composition—SnO₂, 49.15; CaO, 36.93; Au, 9.9. This composition varies in each experiment and depends on the quantity of lime and metals volatilised in the electric furnace. But it has the properties of the purple of Cassius, and on being freed from the lime by hydrochloric acid gives the well known colour. By

volatilising gold with different metallic oxides, the author has been able to vary the purple, and his experiments confirm Debray's ideas on the constitution of the purple of Cassius which showed that it had no definite composition, being merely a lacquer of tin coloured by a fine layer of gold. The presence of graphite is due to the fact that gold at high temperatures dissolves it, and the author has performed experiments to test this by boiling gold in a carbon crucible and then plunging it into cold water. On examination of the cooled contents, crystals of graphite were found in it. *Conclusions.*—Gold distils readily in the electric furnace at a temperature above that of copper and below that of lime. In the alloys with copper and tin, these metals distil before the gold, and from the latter alloy purple of Cassius is obtained, which can be varied in colour by using different oxides.

Two Iodo-mercurates of Lithium.—A. Duboin.

A New Compound: Fluoride of Bromine, BrF₃.—Paul Lebeau.

MEETINGS FOR THE WEEK.

TUESDAY, 16th.—Royal Institution, 5. "Impressions of Travel in China and the Far East," by Prof. Edward H. Parker, M.A.

WEDNESDAY, 17th.—Society of Arts, 8. "The Scientific Aspects of Voice Development," by Dr. W. A. Aiken. Microscopical, 8. Annual Address of the President—"The Life and Works of Bernard Renault."

THURSDAY, 18th.—Royal Institution, 5. "Shakespeare," by the Rev. Canon Henry Charles Bechings, M.A., &c. Society of Arts, 4.30. "The City of Calcutta," by Charles E. Buckland.

Society of Arts, 8. (Howard Lecture). "High Speed Electrical Machinery, with special reference to Steam Turbine Machines," by Prof. Silvanus Thompson, F.R.S.

Chemical, 8.30. "Refractive Indices of Crystallising Solutions, with especial reference to the Passage from the Meta-stable to the Labile Condition," by H. A. Miers and F. Isaac. "Determination of Available Plant Food in Soils by the Use of Weak Acid Solvents," by A. D. Hall and A. Amos. "Action of Ammonia and Amines on Diazobenzene Picrate," by O. Silberrad and G. Rotter. "Preparation of *p*-bis-Triazobenzene," by O. Silberrad and B. J. Smart. "Gradual Decomposition of Ethyl Diazoacetate," by O. Silberrad and C. S. Roy. "Studies on Nitrogen Iodide—Part III., Action of Methyl and Benzyl Iodides," by O. Silberrad and B. J. Smart. "Silicon Researches—Part X., Silicon Thiocyanate," by J. E. Reynolds. "Relations between Absorption Spectra and Chemical Constitution—Part I., The Chemical Reactivity of the Carbonyl Group; Part II., Quinones and α -Diketones," by E. C. C. Baly and A. W. Stewart. Part III., "The Nitroanilines and the Nitrophenols," by E. C. C. Baly, W. H. Edwards, and A. W. Stewart. "Halogen Derivatives of Substituted Oxamides," by F. D. Chatterway and W. H. Lewis. "Effect of Constitution on the Rotatory Power of Optically Active Nitrogen Compounds" (Part I.), by Miss M. B. Thomas and H. O. Jones. "Methyl Benzene Sulphonate and Menthyl- β -naphthalene Sulphonate," by T. S. Patterson and J. Frew. "Apparatus for the Continuous Extraction of Liquids with Ether," by R. S. Bowman. "Action of Bromine on Benzene-*o*-nitrophenol," by J. T. Hewitt and N. Walker. "Some Reactions and New Compounds of Fluorine" (Part I.), by E. B. R. Priceaux. "Contributions to the Chemistry of the Rare Earths" (Part I.), by M. Esposito. "Synthesis of Aldehydes by Grignard's Reaction," by G. W. M. Williams. "Condensation of Dimethylidihydroresurin and of Chloroketodimethyltetrahydrobenzene with Primary Amines—Part I., Monamines, Ammonia, Aniline, and *p*-Toluidine," by P. Haas.

FRIDAY, 19th.—Royal Institution, 9. "Some Applications of the Theory of Electric Discharge to Spectroscopy," by Prof. J. J. Thomson, F.R.S., &c.

SATURDAY, 20th.—Royal Institution, 3. "The Church in France," by J. E. C. Bodley.

THE CHEMICAL NEWS.

VOL. XXIII., No. 2408.

NEW RESEARCHES ON THE ATOMIC WEIGHT OF NITROGEN.*

By PHILIPPE A. GUYE.

(Continued from p. 14).

Volumetric Analysis.

A GLASS vessel containing an iron spiral, analogous to that used for the gravimetric analysis, is connected with a mercury manometer, in which the mercury is brought up to a certain level so as to operate at constant volume.

The vessel after being filled with nitrous oxide is surrounded with ice, and the initial pressure registered. The ice is then removed, and the oxide decomposed by raising the spiral electrically to a red-heat. After cooling, the pressure of the nitrogen is reduced to o^2 , a slightly higher pressure than the initial one. After all corrections for the compressibility of the gases and the difference of temperature of the space required have been made, the excess of the pressure obtained above the initial pressure of 760 m.m. of mercury was found equal to the following values:—

TABLE XIV.

Pressures reduced to o^2 .		Increase for 760 m.m.
N ₂ O.	N ₂ .	
745·93	751·37	5·60
764·90	770·29	5·30
767·72	773·26	5·43
762·97	768·49	5·45
Mean..		5·44

It has been found that the mean 5·44 should be subjected to a small correction, from the fact of the diminution of capacity of the glass vessel due to the transformation of part of the iron of the spiral into iron oxide. This correction brings the number from 5·44 to 5·21 m.m.

The ratio of the volumes of the two gases N₂:N₂O is therefore—

$$\frac{N_2}{N_2O} = \frac{765.21}{760.00} = 1.00686.$$

The extreme values are—

$$1.00707 \text{ and } 1.00667,$$

the difference being 4/10000 only, corresponding probably to a slight uncertainty of 1/5000 on the mean.

Adopting for the densities of the gases, nitrogen and nitrous oxide, the mean of all the found values, we have deduced that:—

	Grms.
1 litre N ₂ O, weighing	1·97772
Contains 1·0068 litre N ₂ , weighing 1·25045 ×	
1·00686	1·25903

And, by difference, a weight of oxygen 0·71869

Whence—

$$N = \frac{16}{2} \frac{1.25903}{0.71869} = 14.015.$$

Allowing, with Jaquero and Bogdan, for an uncertainty of 1/10000 on the densities of N₂ and N₂O, and of 2/10000 on the volume ratio, the error on the atomic weight of nitrogen would be 7/10000 if these causes of error act in the same direction, and 1·7/10000 if they compensate as well as possible, giving as mean 4·4/10000.

The possible error ΔN resulting on the atomic weight of nitrogen will be—

$$\Delta N = \pm \frac{14 \times 4.4}{10000} = \pm 0.0067.$$

The two methods—gravimetric and volumetric analysis—afford, therefore, under the given conditions, sufficient accuracy to determine the second decimal of the atomic weight of nitrogen.

The result to which we have been led has also been recently confirmed by the complete analysis of a second oxide of nitrogen, the dioxide by Gray. In his first notice he announced that he had effected the complete analysis of this gas by fixing the oxygen with nickel, and condensing the nitrogen upon charcoal cooled to the temperature of liquid air. This process therefore presents great similarity to those employed in my laboratory for the analysis of the suboxide. The mean of six analyses led Gray to the value—

$$N = 14.006,$$

which he explains as "probably a little too low."

Placing together the physico-chemical and gravimetric methods, we are led to the following recapitulation:—

TABLE XV.—General Recapitulation.

A. Physico-chemical Methods.		N.
Ratio	N ₂ :O ₂ (6 values)	14·009
"	N ₂ :CO (6 values)	14·006
"	N ₂ O:CO ₂ (2 values)	14·007
"	NO:O ₂ (2 values)	14·008
Physico-chemical mean (4 ratios) ..		14·008
B. Gravimetric Methods.		
Analysis by weight of N ₂ O (5 expts.)		14·007 (G. and B.)
" by volume of N ₂ O (4 expts.)		14·015 (J. and B.)
" by weight of NO (6 expts.)		14·006 Gray
Gravimetric mean (3 ratios) ..		14·009
General mean		14·0085
Most probably		14·009

In the face of such complete agreement between the means of the two groups of methods, which only make use of the direct ratios to oxygen, or to compounds relatively rich in oxygen, it is certainly logical to renounce the old value $N = 14.04$ or 14.055 of Stas' experiments, in favour of either the mean—

$$N = 14.009$$

or the round number—

$$N = 14.01,$$

which only differs from the preceding one by 1/14000.

One might even use the value $N = 14.00$ which many chemists have continued to use; the error thus committed is less than that recently discovered by Richards in the atomic weight of sodium.

V. Conclusions and Consequences.

Recent researches clearly point to the revision of the atomic weight of nitrogen in the direction which brings it almost to the value that Marignac, in 1843, considered as the most probable.

This revision carries with it an important consequence to which I would draw your attention.

If the methods employed by Stas, his forerunners, or his successors, do not admit to-day of sufficient accuracy to ascertain the second decimal of the atomic weight of nitrogen, it is none the less true that the mean of these numerous experiments approximates to $N = 14.04$; the extreme values of all the means are, according to Clarke (1897), $N = 14.017$ and $N = 14.053$. According to the laws of large numbers, this result is only compatible with an exact value, $N = 14.009$ or $N = 14.01$, if the atomic weights

* From the Bulletin de la Société Chimique de Paris, 1905.

considered known by the old methods are a little too high. I say a "little" because calculation shows that very slight errors in these atomic weights become considerably multiplied in arriving at nitrogen. An error of this kind can be demonstrated with sodium, the atomic weight of which, fixed by Stas at $\text{Na} = 23.043$, becomes, by the researches of Richards, $\text{Na} = 23.008$ (for $\text{Ag} = 107.93$) or $\text{Na} = 23.006$ (for $\text{Ag} = 107.92$). It is therefore of the highest interest that this work of revision should be carried out in a very complete manner.

It is to be foreseen that if one is led, in the course of these researches, to raise somewhat the values of certain atomic weights, as recently in the case of chlorine and iodine, other atomic weights will have to be lowered by nearly as much.

(To be continued).

THE PHYSICAL AND CHEMICAL PROPERTIES OF IRON CARBONYL.*

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S.,
Jacksonian Professor in the University of Cambridge,

and
HUMPHREY OWEN JONES, M.A., D.Sc., Fellow of Clare College, and Jacksonian Demonstrator in the University of Cambridge.

(Concluded from p. 15).

Decomposition by Light.—Mond and Langer (*loc. cit.*) state that liquid iron carbonyl is rapidly decomposed by light, giving rise to a solid product and carbon monoxide. Determinations of the percentage of iron in the compound made by them indicated that the formula was $\text{Fe}_2(\text{CO})_7$, but the body was not obtained in a pure state. This behaviour to light constitutes the most striking difference between the carbonyls of iron and nickel, and was therefore examined more fully.

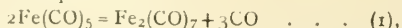
The decomposition was first investigated over mercury in a barometer tube. A weighed quantity of liquid iron carbonyl in a sealed bulb was introduced into a barometer and the bulb was then broken, after which the tube was exposed to light.

In the laboratory on bright days in February the decomposition was extremely slow, but on the same days in direct sunlight the decomposition was rapid and the evolution of gas was completed in a few hours. Exposure to the electric arc only induces the change very slowly, and a strong acetylene flame is almost without action. The volume of gas evolved (which was found to be pure carbon monoxide) was then measured and the solid collected. The solid was found to consist of beautiful, lustrous, hexagonal plates of an orange colour which, when pure, retained their lustre for a very long time on exposure to ordinary air, and indefinitely in dry air. If, however, the decomposition had not been completed and the solid was contaminated with traces of the liquid compound, rapid change occurred and the compound sometimes took fire.

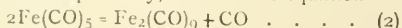
The following are two typical examples of experiments made in this way:—

1. 0.0905 grm. iron carbonyl gave 4.7 c.c. of carbon monoxide.
2. 0.2970 grm. iron carbonyl gave 18.4 c.c. of carbon monoxide.

According to the equation—



there should have been produced 15.5 c.c. and 50.9 c.c. of carbon monoxide respectively, whereas the equation—



requires 5.2 c.c. and 17 c.c. of carbon monoxide respectively.

It would, therefore, appear that the formula of the solid compound is $\text{Fe}_2(\text{CO})_9$ and not $\text{Fe}_2(\text{CO})_7$, and that the decomposition induced by light is represented by equation 2 above. This result was confirmed by carrying out the

decomposition in a large glass bulb out of contact with mercury.

A small sealed bulb filled with iron carbonyl was introduced into a large glass bulb, which was then sealed on to a glass tap, dried carefully, and exhausted with a Töpler pump. The small bulb was then broken and the whole exposed to light for some days, after which the carbon monoxide was pumped out and measured. In these experiments it was practically impossible to get the decomposition completed, since the bulb became covered with a deposit of the solid, which cut off the light.

The following are typical examples:—

- 0.6006 grm. of the liquid carbonyl gave 33.2 c.c. of carbon monoxide and left 0.501 grm. of solid. Theory requires 34.3 c.c. of gas and 0.557 grm. of solid.

- 0.5076 grm. gave 32 c.c. of gas. Theory requires 33.8.

Decomposition was incomplete, as shown by behaviour of solid, and by the fact that on admitting air to the carbon monoxide a deposit of iron oxide was produced. Another type of experiment also served to confirm the above conclusively:—

A carefully dried glass bulb of about 250 c.c. capacity was fitted with a small mercury manometer, thoroughly exhausted, and filled with dry iron carbonyl vapour, the pressure of which was measured at a definite temperature. The bulb was then exposed to light until no further change took place; after the bulb had been brought to the original temperature, the pressure was found to have been reduced to one-half its former value, as required by equation 2 above.

None of the specimens of the solid carbonyl prepared by either of the foregoing methods was found to be pure enough to give good results on analysis. The specimens prepared over mercury always retained small globules of mercury too small to be visible, but whose presence became evident during combustion, while the specimens prepared in glass bulbs were always contaminated with a little of the liquid, which either caused spontaneous combustion of the sample or decomposed quietly and left some oxidation product poor in carbon. The percentages of carbon monoxide obtained were too high for $\text{Fe}_2(\text{CO})_7$, 63.6 per cent, and too low for $\text{Fe}_2(\text{CO})_9$, 69.2 per cent; thus, for example, 65.0 and 66.5 per cent of carbon monoxide were obtained in two combustions.

We, therefore, examined the decomposition of the liquid in various solvents and succeeded in obtaining the compound in a pure state.

Iron pentacarbonyl dissolved in dry ether or petroleum ether and exposed to sunlight, undergoes rapid decomposition with evolution of carbon monoxide and formation of large reddish orange crystals of the solid carbonyl. To obtain the pure solid compound in quantity, the solution was sealed up in a dried and exhausted glass tube and exposed to light. Owing to the unavoidable exposure to air during the transference, a small amount of a precipitate of an oxidation product was sometimes produced. When a quantity of the solid carbonyl had been formed, the tube was opened (a considerable pressure of carbon monoxide was always produced), and the precipitate was removed easily by shaking the tube and pouring off the liquid, when the precipitate—which is very light and settles slowly—is poured off with the liquid, and the crystals remain behind. The crystals were then washed two or three times with the solvent and rapidly transferred to a desiccator containing sulphuric acid and solid paraffin. When prepared in this way they retain their lustre, and show no signs of change for a long time on exposure to air.

The percentage of carbon monoxide was then determined by combustion, using the same precautions as in the case of the liquid. The method of estimating the iron after decomposing the solid by heating in a sealed tube with bromine water was found unsatisfactory, and after trying several methods it was found that, if the compound were dropped slowly into pure nitric acid in a weighed

* A Paper read before the Royal Society, November 16, 1905.

crucible, complete decomposition took place, with effervescence and without loss of iron. The resulting liquid was then evaporated to dryness on a water-bath, the ferric nitrate decomposed by careful ignition, and the ferric oxide weighed.

The following results were obtained by these methods:—

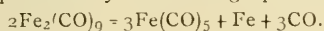
1.	0.2470	gram.	gave	0.2655	gram.	CO ₂ .
2.	0.3178	"	"	0.3417	"	"
3.	0.1839	"	"	0.1992	"	"
4.	0.5791	"	"	0.2534	gram.	Fe ₂ O ₃ .
5.	0.3450	"	"	0.1515	"	"

Found—

	CO.	Fe.
1	68.4	—
2	68.4	—
3	68.9	—
4	—	30.6
5	—	30.7
Fe ₂ (CO) ₇ requires	63.60	36.40
Fe(CO) ₄ ..	66.66	33.33
Fe ₂ (CO) ₉ ..	69.20	30.80

The solid compound is, therefore, Fe₂(CO)₉, or *diferro-nona-carbonyl*. The solid prepared in this way forms large hexagonal plates, often 3 or 4 m.m. in breadth, but always rather thin. It is very sparingly soluble—in fact, practically insoluble—in ether, petroleum-ether, and benzene, but is slightly soluble in methylal, alcohol, and acetone, and much more soluble in pyridine to form a reddish solution. When dissolved the compound becomes much more sensitive to air and moisture, and deposits a reddish precipitate. We have not yet succeeded in re-crystallising the compound. The crystals are slightly dia-magnetic, but less so than the liquid. The density of the solid at 18° C. is 2.085, and its molecular volume is, therefore, about 174. If two grammes-molecules of solid Fe(CO)₅ were converted into Fe₂(CO)₉, then 256 volumes would become 174, or a contraction of about 33 per cent would ensue.

On heating solid iron carbonyl, as stated by Mond and Langer, liquid iron carbonyl is produced, and some solid, probably iron, is left. We find that this change takes place at about 100° C. Under a pressure of carbon monoxide up to 150 atmospheres, there is no rapid change below 95° C., but at this temperature the solid is completely converted into liquid iron carbonyl, though traces of a yellowish-brown solid are sometimes left. Quantitative experiments were made on the decomposition at 100° C. in a stream of hydrogen, and showed that the decomposition could be represented by the following equation:—



Liquid iron carbonyl, when exposed to light under a pressure of 75 to 125 atmospheres of carbon monoxide in the tube of a Cailletet pump, decomposes without any apparent diminution of the rate of transition. For this purpose the liquid was placed in a small tube kept in position by a plug of glass-wool, so that the liquid never came in contact with the mercury. If, however, the sealed tube containing liquid iron carbonyl, or a solution of it in ether, be heated to any temperature between 60° and 100° C., while exposed to light, no solid separates even after several hours, whereas below 50° C. solid is formed in about half an hour. This is also true when the liquid is under a pressure of 50 to 100 atmospheres of carbon monoxide. The solution which had been exposed to light at a temperature above 60° C. even on cooling gave no deposit of solid, showing that no decomposition had been caused by the action of light at these temperatures. And this is confirmed by the fact, which will be proved later, that if solid had been produced in solution it would at this temperature have formed a solution of an intense green colour.

The decomposition of liquid iron carbonyl dissolved in ether, amylene, or petroleum-ether (B.P. 30° to 40° C.) by light, takes place slowly at the temperature of liquid

air. The solutions become solid, and, after exposure to sunlight for about three hours inside a vacuum vessel of liquid air, and then allowing to warm up in the dark, a faint deposit of solid was observed.

In spite of the fact that pressure is not effective in preventing the decomposition by light, the reaction is reversed slowly under a slight pressure of carbon monoxide at the ordinary temperature in the dark. Tubes containing iron carbonyl alone, or in solution, which had been exposed to light so that they contained some of the solid carbonyl, on standing at the ordinary temperature in the dark for some weeks, were found to contain no solid; so that the solid had absorbed the carbon monoxide which had been evolved, and had been completely re-converted into the liquid. These observations are of considerable interest and importance in their bearing on the question as to whether the action of light is exothermic or endothermic. If the light reaction is not endothermic, then we must assume the action of carbon monoxide on the solid carbonyl, and the change backwards into the liquid carbonyl is attended by an absorption of heat. Further experiments must be made to settle the question.

When solid iron carbonyl is heated alone, as stated above, no change takes place below 100° C.; at this temperature a solid and a green liquid are formed. But if the solid be heated with liquids such as ether, petroleum-ether, or toluene, change begins at about 50° C., the solid decomposes, and the liquid acquires an intense green colour. The intensity of the green colour is so great that the solutions are almost opaque, even in thin layers: in more dilute solutions the absorption spectrum showed a distinct band in the yellow. These green solutions, on exposure to light, again deposit yellow crystals of the solid carbonyl, and become colourless.

In order to determine what kind of light was most effective in inducing this decomposition, small tubes containing a 10 per cent solution of iron pentacarbonyl in ether were exposed in different parts of a solar spectrum and also to sunlight under different coloured screens. It was found that most rapid decomposition occurred in the blue, then green, closely followed by yellow, and lastly red: exposure under red glass produces roughly about one-tenth the amount of solid produced under blue glass in the same time.

Exposure of the liquid in quartz tubes to the electric arc causes slow decomposition only, and the acetylene flame is still less active.

Colouring the ether solution with dyes was also tried; cyanine and chlorophyll allow rapid decomposition, azobenzene retards the decomposition slightly, isatin and alizarine somewhat more.

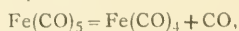
It has already been stated above that the decomposition occurs readily in solution in petroleum-ether and ether; the same is true of alcohol; in pure benzene the decomposition appears to be slower, but if the benzene contain traces of thiophene a black solid is deposited. Solutions of iron carbonyl in pyridine become dark red in colour when exposed to light, gas is evolved, but no solid is deposited except from strong solutions of about 50 per cent by volume. This is to be accounted for by the solubility of the solid in pyridine. Carbon bisulphide and nitrobenzene, which do not react with iron carbonyl in the dark, when exposed to light react with the formation of solid precipitates.

The most striking result observed was with solutions of iron carbonyl in nickel carbonyl. These solutions are of a much paler yellow colour than solutions of equal concentration in other solvents. Thus, for example, a 10 per cent solution of iron carbonyl in ether has just the same intensity of colour as a 30 per cent solution in nickel carbonyl. A 10 per cent solution deposits no solid after exposure to bright sunlight for several weeks, a 25 per cent solution (by volume) deposits no solid from the liquid, but solid is deposited in the vapour space above the liquid; a 50 per cent solution deposits some solid both in the liquid and in the vapour space.

That no decomposition occurs in dilute solutions of iron carbonyl in nickel carbonyl is shown by the facts that no gas is evolved from these solutions, and that solid iron carbonyl is only sparingly soluble in nickel carbonyl. The absence of any change is not to be accounted for by the absorption of the active light by the nickel carbonyl, since the iron carbonyl has been shown above to be sensitive to light in the visible part of the spectrum which is not absorbed by nickel carbonyl. This fact was further confirmed by exposing a small tube full of iron carbonyl immersed in liquid nickel carbonyl to light, when decomposition was found to take place rapidly.

The following may be suggested as a simple hypothesis to account for the unique behaviour of nickel carbonyl as a solvent of iron carbonyl:—

The initial action of light on iron carbonyl might be represented by the equation—



the hypothetical iron tetracarbonyl produced may be assumed to combine at once with a molecule of iron pentacarbonyl to produce the solid nonacarbonyl, thus:—



If this molecular mechanism of the light reaction be admitted, then there is no reason why iron pentacarbonyl may not form an analogous body of feeble stability by combining directly with nickel tetracarbonyl, thus:—



A compound of this kind, though unstable in itself (since the vapour above the solutions contains iron carbonyl and the concentrated solutions deposit some solid), may yet be unacted upon by light. The existence of this compound is rendered probable by the fact that solutions of iron carbonyl in nickel carbonyl have such a pale colour compared to solutions of the same concentration in other solvents.

The observations on the action of light on iron carbonyl under different pressures of carbon monoxide, at different temperatures and in solution in various solvents, will be continued as soon as the necessary sunlight is available.

DISTILLED WATER SUPPLY FOR "WORKS" LABORATORIES.

By RICHARD SELIGMAN.

IN a "works" laboratory an adequate supply of distilled water is always a matter of importance, and in those situations where cheap gas is not available, its provision is often attended with considerable difficulty. When works are provided with steam it is a simple matter to obtain distilled water by running a pipe into the laboratory, and passing the steam through a condensing coil, but this method is not available where condensing engines are in use, or where the feed water is charged with volatile matter, for the condensed water will contain oil or other impurities.

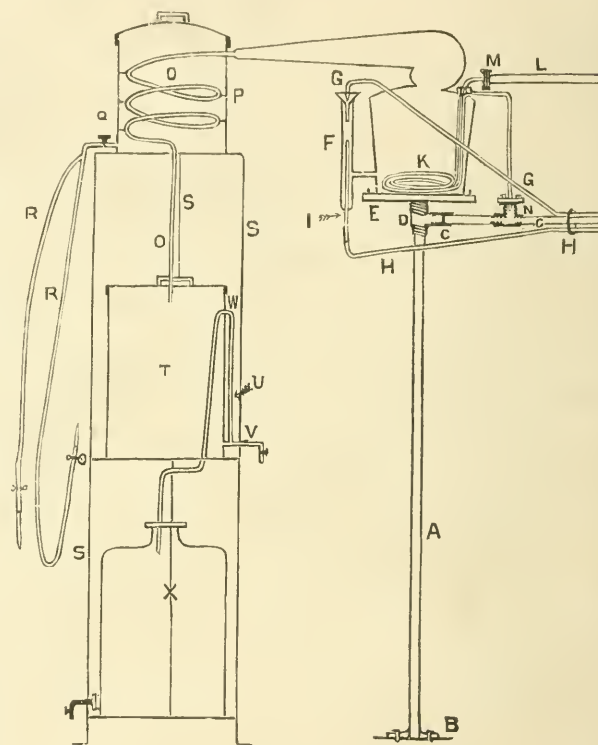
If a large number of analyses are made every day it generally happens that the glass wash-bottle does not meet the requirements of the worker. Not only has it to be frequently replenished and heated on a separate stove, but it is liable to breakage, and the process of washing, say, twenty or thirty precipitates with it is exceedingly laborious and slow. It is found convenient to supplant the wash-bottle by an elevated tank from which passes a suitable number of rubber tubes long enough to reach all parts of the bench. To the ends of the tubes are attached suitable glass nozzles. Each tube is closed by a pinch-cock on compressing which a stream of water issues from the nozzle, and may be used to expeditiously wash a large number of precipitates. The water in the tank is kept at the required temperature by a steam coil or by a stove.

For the complete installation the pieces of apparatus necessary are:—

1. Still.
2. Condenser.
3. Receptacle for condensed water.
4. Elevated tank supplied with a heating coil.

The following arrangement, which has given satisfactory results in daily use, and which can be cheaply and easily installed, has the great advantage that it can be made from apparatus with which most works laboratories are already provided.

Where the working bench is in the middle of the laboratory, so that both sides are utilised, economy of space is desirable. The still is therefore supported on an upright of $\frac{1}{2}$ -inch iron (A) 3 feet 6 inches long, firmly screwed to the



bench-top by means of a flange (B). This structure is steadied by the waste-steam pipe (C), which crosses from the wall at a convenient height above the heads of the operators. On the top of A is a T-joint (D) into which the plugged end of C is screwed, and which also carries the platform (E), on which rests the still. The still has a capacity of five litres, and has a constant level supply (F), to which the water is brought by a $\frac{3}{8}$ -inch compo-pipe (G) carried along the steam pipe C. The overflow is carried off by the pipe (H) likewise suspended from C. The pressure in the still is regulated by adjusting the height of the pipe (I), which at the same time acts as a safety valve. Heat is supplied by a flat coil (K) of $\frac{3}{8}$ -inch copper pipe, tinned outside, of which three turns are found to suffice. The coil hangs $\frac{1}{2}$ -inch above the bottom of the still. Live steam from the boilers is supplied by the pipe (L), joined by the coupling (M) to the coil K. The waste steam passes by the coupling (N) to a branch on the pipe C, which in its turn is closed by a steam trap of any suitable form. The neck of the still is soldered into the mouth of the block-tin condensing worm (O), which makes three turns inside the copper tank (P). This latter is $8\frac{1}{2}$ inches in diameter and

9½ inches high, is well tinned inside, and serves the double purpose of condenser and supply tank.

It is filled once a day with distilled water, and the steam passing through *o*, whilst being condensed itself, heats the water surrounding it, and maintains it at a suitable temperature for use. Close to the bottom of *P* is the tap (*q*), to the neck of which the rubber tubes (*RR*) carrying pinch-cocks and glass nozzles are attached. The tank *P* stands on the tripod (*s*), 4 feet above the bench. A second stage in this tripod carries the tinned copper tank (*T*) (8½ inches in diameter by 14 inches high), into which the hot water delivered by the worm, *o*, falls. Close to the bottom of *T* is a T-shaped pipe (*v*). The upright arm carries a glass tube (*U*), the horizontal arm a tap for drawing off the cold water in the bottom of *T*. *U* serves the double purpose of gauge and overflow, being bent back on itself at *w*, and delivering into the bottle (*x*). In order to prevent syphonage, a minute hole is blown in *U* at the top of the bend *w*. Thus only cold water flows into *x*.

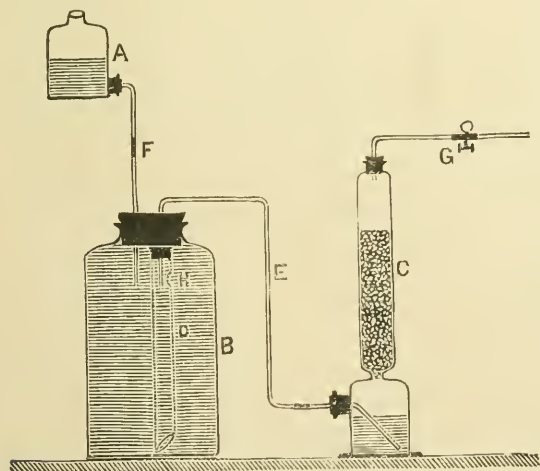
The apparatus described works automatically, except that each day the bottle *x* has to be removed, and its contents emptied into the tank *P*. It gives a supply ample for about 200 analyses weekly, as well as for those other purposes requiring the use of distilled water.

A NEW FORM OF GAS GENERATING APPARATUS.

By A. W. GREGORY.

THE apparatus here described has been found very efficient for large and continuous supplies of sulphuretted hydrogen.

A is a tubulated bottle placed in an elevated position, *F* a delivery tube leading from *A* to the reservoir bottle *B*, which is simply a wide-mouth bottle of about five litre capacity.



D is a wide glass tube connected with *E* by means of a cork and has an opening at *H*, just above the termination of *E*.

C is a "tower," the upper part of which is filled with iron sulphide.

A and *B* are filled with dilute hydrochloric acid and the clip *G* opened.

Acid flows into *C*, and sulphuretted hydrogen is generated. When the clip is closed, the partially spent and denser acid returns to *B*, and is conducted to the bottom of the reservoir by means of the tube *D*.

On again opening the clip, fresh acid goes to the tower through the opening *H*.

Each time the clip is opened the acid of lowest specific gravity and, consequently, the strongest acid in the reservoir, is brought into contact with the iron sulphide.

THE CHEMICAL SEPARATION OF THE RADIO-ACTIVE TYPES OF MATTER IN THORIUM COMPOUNDS.*

By HERMAN SCHLUNDT and RICHARD B. MOORE.

Continued from p. 17).

Curves of Recovery and Decay (continued).

THE far greater increase in activity exhibited by the residues obtained in the pyridine and fumaric acid separations—the residue from the latter showing an increase of more than 50 per cent over the initial value—demands further explanation. Moreover, the fact that the maximum values are reached in about one-fourth the time required for the ammonia residue to come to a maximum, indicates that the distribution of the several types of matter in the separation with fumaric acid and pyridine differs in some respects from the separation by means of ammonia. It will be shown that this difference arises from the matter causing imparted activity—the fumaric acid and pyridine effecting a separation of its components. From his experiments on the matter causing imparted activity of thorium (*Phil. Mag.*, 1903 [6], v., 95), together with the experiments carried out by Rutherford and Miss Brooks ("Radio-activity," p. 260), Rutherford concluded that the imparted activity was complex. On the basis of the results obtained by exposing a negatively-charged wire for short intervals to the thorium emanation, Rutherford pointed out that they could be satisfactorily explained by assuming the presence of two products—one not radio-active, that is, emitting no rays, with a rapid rate of change, the other resulting from it, radio active, but with a slower rate of change. In the first change, one-half of the matter disintegrates in fifty-five minutes, in the second one-half changes in eleven hours. Quite recently, however, Rutherford (*Phil. Trans.*, A., 376) has stated that the results obtained might be explained equally well by assuming that the matter with the slow rate of change and giving off no rays is the first product, and that this inactive matter produces a radio-active product with the rapid period of decay. About the same time Miss Slater (*Phil. Mag.*, May, 1905) succeeded in effecting a partial separation of the two types of matter constituting the imparted activity, which had been deposited on a negatively-charged wire by a long exposure to the emanation from thorium. She did this by the action of the cathode rays and also by heating to a high temperature. The results of her experiments, Miss Slater states, can be satisfactorily explained on the theory, independently advanced by her, that the first product is inactive and has the slow period of decay, and that it changes into a radio-active product with a rapid period of decay. Miss Slater designated the first product, which emits no rays and has the slow rate of change, *ThA*, and the second product which emits radiations and has the rapid rate of decay, *ThB*. We shall use this terminology in connection with the further discussion of the initial peculiarities of the curves of recovery and decay. The view advanced by Rutherford and Miss Slater also affords a satisfactory explanation for the initial irregularities in the curves of recovery and decay of the precipitates and residues obtained in the separations with fumaric acid and pyridine.

When thorium is precipitated with fumaric acid, the precipitate, instead of containing both *ThA* and *ThB*, as is the case when the precipitation is made with ammonia, contains only *ThB*. The first product of the imparted activity, *ThA*, is soluble in excess of this reagent, and

* From the *Jou-nai of Physical Chemistry*, ix., No. 8, p. 682.

hence is found in the filtrate with ThX. As ThA undergoes change without giving off rays, the initial activity of the filtrate has the same value as that obtained with ammonia. The precipitate, which contains thorium and ThB, is not in radio-active equilibrium, but before the thorium has formed even a few per cent of ThX, ThB has changed practically completely into a final inactive product, one-half of the change taking place in fifty-five minutes. Hence, as ThB is responsible for about one-half the ionisation produced by the precipitate initially, its rapid decay accounts for the rapid decrease in activity of the precipitate during the first four hours after precipitation. It will be noted that by deducting the effect due to the non-separable activity from the curve representing the combined effect of the non-separable thorium activity and ThB (Curve c, Plate II.), the difference curve drops to half value in about one hour, which is the characteristic rate of decay of ThB.

From the above it can readily be seen that if the processes of precipitation and filtration are carried out slowly, so that the first readings are made four or five hours after the first precipitation, the curves will show no initial drop, and the result will be the same as that obtained by Rutherford and Soddy with twenty-three precipitations by means of ammonia.

In the residue from the filtrate ThX and ThA are in equilibrium at the outset, but the residue as a whole is not in equilibrium, owing to the absence of the radio-active product ThB. This product, however, is produced from ThA at a much faster rate than ThX decays, and since ThB changes at a still faster rate, the activity of the residue shows a rapid initial rise, reaching a maximum about five hours after separation.

The residue obtained in the ammonia separation being free from both ThA and ThB shows a smaller rise initially, because the ThA produced by ThX is very small in proportion to that present in the fumaric acid residue, and since the increase in activity of the residue depends upon the amount of ThB produced from ThA, it follows on this view that the initial increase in activity should be considerably greater when the residue contains the normal amount of ThA, as is the case in the fumaric acid separation.

The initial peculiarities of the curves representing the decay and recovery of the products obtained in the pyridine separation are not quite as marked as in the fumaric acid separation, probably because the separation of ThA and ThB was not quite complete.

The correctness of the view here presented was tested by several experiments. In connection with the fumaric acid separation in the early part of this paper, two methods were given by which ThA was separated from the other products. In one of these experiments, ThA was removed from the precipitated thorium, obtained with ammonia, by means of fumaric acid, and in the other one, ThA was removed from the filtrate obtained in the fumaric acid precipitation by the addition of ammonia. The curve marked ThA $\rightarrow$ ThB, Plate I., is the theoretical curve of the residue ThA, while the plotted points represent the experimental values obtained. It will be observed that this curve closely resembles the initial portion of the curve of the fumaric acid residue (C, Plate II.).

In another experiment the thorium was precipitated once with fumaric acid and filtered off; the precipitate was then quickly re-dissolved in dilute nitric acid, and after the addition of a trace of lead nitrate, the solution was at once subjected to electrolysis for five minutes, a rotating cathode being employed with a current density of about six amperes per 100 sq. cm. of cathode surface. The electrodes were washed and dried quickly and then tested for activity. The slight deposit of lead peroxide on the anode was found to be practically inactive and subsequently showed no change, but the slight deposit on the cathode was highly radio-active, its activity decreasing according to an exponential law, decaying to half value in fifty-five minutes, and finally becoming entirely inactive

and remaining so. This experiment shows that the precipitate of thorium obtained with fumaric acid contains the product ThB, and not ThA: for, according to the experiments of Pegram (*Phys. Rev.*, 1903, xvii., 424) on the electrolysis of thorium nitrate solutions, ThA is deposited on the anode under the conditions of our experiment, but the anode deposit in our experiment was inactive, and showed no change with the time, as it should have done if ThA had been deposited. Our thorium nitrate solutions, when subjected to electrolysis, behaved in the manner described by Pegram—the anode deposit being quite active, the activity decaying to half value in eleven hours after showing the initial rise characteristic of ThA, while the cathode deposit had a slightly slower rate of decay than the ThB similarly obtained from the thorium nitrate solution from which ThA and ThX had been removed.

(To be continued).

CITY AND GUILDS OF LONDON INSTITUTE.

FINSBURY TECHNICAL COLLEGE PAST STUDENTS' DINNER.

ON Saturday last, the 13th inst., Prof. MELDOLA, F.R.S., took the chair at the first Annual Dinner of the Past Chemical Students of the Technical College, Finsbury, at the Hôtel Previtali.

In addition to the Lecturers and Demonstrators of the Chemical Department, 70 Past Students gathered together, including Dr. M. O. Forster, F.R.S., Dr. G. T. Moody, Dr. O. Silberrard, Dr. C. H. Desch, Messrs. A. R. Ling, J. L. Baker, F. G. Collier, T. J. Underhill, A. Greeves, F. H. Cair, and many others. The Principal of the College, Prof. Silvanus P. Thompson, F.R.S., was prevented by ill-health from being present, and Prof. W. J. Pope, F.R.S., was among the past students who were unable to come.

Prof. MELDOLA referred with pride to the number of past students, who had won distinction in the chemical world, who were gathered around him; Finsbury was one of the earliest Technical Colleges, and had a record of a quarter of a century's usefulness to the technical industries of the country.

Dr. MOODY, who proposed "The College," said that this year was a most appropriate one for the first Annual Dinner, as their head, Prof. Meldola, now held the highest distinction the Chemical Society had to offer, the office of President.

A well-chosen musical programme added to the success of the evening.

OBITUARY.

DR. HERMANN JOHANN PHILIPP SPRENGEL, Ph.D., F.R.S.

WE regret to announce the death of Dr. Hermann Sprengel, which occurred suddenly on Friday last, the 12th inst., at the age of 72.

Dr. Sprengel was born in the year 1834 at Schillerslage, near Hanover, in Germany, and was educated at the Universities of Göttingen and Heidelberg, where he took his degree in 1858. Coming to England in the following year he worked first at Oxford, and then at the College of Chemistry, Guy's and Bartholemew's Hospitals. The most important of his researches were concerned with the two extremes of the gaseous state of matter, viz., high vacua and detonating agents, but it is by the well-known Sprengel mercury pump that his name will be best remembered, and were it not for this discovery it is highly probable that electric lighting would not be in such an advanced stage as it now is, to say nothing about other researches on radiant matter, X-rays, electrons, &c., which have depended to such a great extent on the perfection of the apparatus used for obtaining high vacua.

NOTICES OF BOOKS.

Elements of Quantitative Analysis. By G. H. BAILEY, D.Sc. (Lond.), Ph.D. (Heidelberg). London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1905.

THERE is much in this little work to commend it both to teachers and students, although in some respects it is not above reproach. To illustrate the former statement, first it is only necessary to call attention to Part II. on Volumetric Analysis, in which well-chosen methods are most carefully described, and, indeed, accuracy of detail is a marked characteristic of the book. Instructive examples are given of the examination of minerals containing the rarer elements, and the description of, for instance, the extractions of uranium from pitchblende and of the rare earths from cerite will be found useful by advanced students. Part I. treats of the general operations with which the beginner should make himself familiar, and the author's attention to detail and minuteness of description should both tend to assist especially those who are working with but little or no assistance from a teacher. Parts III. and IV. are devoted to the Analysis of Minerals, many of which are studied, and to Technical Products, a few typical analyses being outlined, such as those of fertilising agents, soap, &c. The chief defect of the book is the comparative neglect of electrolytic methods, with the exception of the estimation of copper and lead, which are very briefly described, although it is now generally recognised that electrolysis provides very often the most accurate and rapid methods of determining some metals, and every student should be given practice in the manipulation of electrolytic apparatus.

Glue, Gelatine, and their Allied Products. By THOMAS LAMBERT. London: Charles Griffin and Co., Ltd. 1905.

THE rapid growth of the glue and gelatine industry makes the appearance of a text-book devoted exclusively to its consideration particularly welcome, and although this work is not very exhaustive, it gives a sufficient account of modern methods of working, chiefly from a practical standpoint, the preparation of glue and gelatine being described fully, while a very valuable collection of recipes for the manufacture of liquid glues, cements, &c., is included. These recipes have been collected from periodical literature, and are believed by the author to be trustworthy. The chapter on the residual products from glue and gelatine gives the manurial values, and composition of fish and bone residues, while the last chapter deals with the analysis of the raw and finished products. This part is in some respects the least satisfactory in a book which is otherwise of real value. For instance, the details of the determination of fat in a Soxhlet's extractor are inadequate, the temperature at which the operation is conducted not being stated, while the number of times of syphoning recommended would probably be found by experience to be insufficient for the complete extraction. It appears ill-advised to include the analysis of manures, unless more space can be devoted to a description of the processes, and the greatest stress must be laid upon the exceedingly unsatisfactory directions given for the preparation of the standard solutions used in volumetric work. As an example, it may be mentioned that to prepare normal sodium hydrate it is suggested that 40 grms. of pure or 42 grms. of ordinary caustic soda should be dissolved, and the solution made up to a litre without any preliminary purification in the latter case, or any standardisation with a more accurately prepared acid solution, while the fact that the value of each c.c. is given to three places of decimals would lead the inexperienced to suppose that a high degree of accuracy might be expected when such a solution was used.

The Book of the Rothamsted Experiments. By A. D. HALL, M.A. (Oxon.). London: John Murray. 1905.

IN this account of the work of Lawes and Gilbert an excellent summary is given of the Rothamsted Memoirs, and the author, writing more especially for agricultural teachers, has emphasised the chief results obtained, and dwelt upon the main purpose of the experiments—to ascertain how the plant grows and how it derives its nutriment from the soil. While the requirements of the teacher are specially kept in view, the author has written so clearly and lucidly that the agricultural student will find nothing in the book above his head, and it will serve to broaden and deepen his knowledge if he reads it in conjunction with the usual text-books. Moreover, the farmer will benefit by the perusal of an account of the most elaborate and complete set of field experiments ever conducted, although he may not find that thus he has actually added to his knowledge of how to manage his own land with the greatest success, for the experimental conditions were purposely often exceedingly unpractical, and the man who takes a strictly utilitarian view of all scientific work would be led to doubt the usefulness in practice of many of the experiments. But the student of deeper insight will recognise the value of this seemingly useless work, by which material has been steadily collected during the past sixty years for the expert to sift and base his opinions upon. The discussion of experiments on feeding is included, besides some miscellaneous researches on sewage irrigation, the composition of the wheat-grain and its mill products, &c., while, naturally, the bulk of the book is devoted to experiments on the growth of various crops, grown either continuously year after year upon the same land, or in rotation. Each chapter is admirably illustrated by curves and diagrams, and summaries are frequently given. The importance of the work of Lawes and Gilbert is being more fully recognised as time goes on, and this general account, by the able director of the station, of the results so far obtained must be acknowledged to be the most complete and interesting which has yet been issued.

Die Elektrolyse Geschmolzener Salze. Zweiter Teil. ("The Electrolysis of Fused Salts." Part II.). By RICHARD LORENZ. Halle-a-S.: Wilhelm Knapp. 1905.

THE second part of this monograph, the twenty-first volume of the series on Applied Electrochemistry, deals with Faraday's law, the migration of the ions, and conductivity. The author has brought together all that is known of these subjects, adding his own observations and explanations, so that the work is of more value than a mere compilation. The order adopted is that of systematic electrochemistry, and as no similar work exists dealing exclusively with the electrochemistry of the fused state, the monograph will be heartily welcomed, especially as it adds considerably to our knowledge of the theory of this branch, which has been, comparatively speaking, neglected. The author is of the belief that the time is not far distant when much quantitative work, performed from theoretical points of view, will be done in this region, and it will be universally recognised, when this time comes, that he has done much to bring about this end, both by his work of investigation, and secondarily by the preparation of this exhaustive monograph on the subject.

Les Quantités Élémentaires d'Electricité. Ions, Electrons, Corpuscules. ("The Elementary Quantities of Electricity. Ions, Electrons, Corpuscles"). Edited by HENRI ABRAHAM and PAUL LANGEVIN. Two Volumes. Paris: Gauthier-Villars. 1905.

THESE volumes belong to the second series of memoirs on physical subjects, issued by the French Physical Society. The papers in it are reproduced in the alphabetical order of the authors' names, the papers of each author being arranged chronologically. This arrangement simplifies reference to the books, and seems on the whole to be the

most convenient. The editors have carefully selected the most important and characteristic papers of all the authors, and the translators have frequently added explanatory notes. In the case of radio-activity the editors have confined themselves to those articles which deal with the emission of the α - and β -rays, and have altogether passed over the study of the transformations which occur in radio-active substances. Similarly in other branches, in order to keep within moderate bounds as regards size, they have been obliged to exercise their discretion in neglecting certain aspects, but this has been done with admirable judgment, and has in no way lessened the value of the book, which contains a collection of all the work that has been published on the nature and properties of ions, electrons, or corpuscles.

Handbuch der Anorganischen Chemie. ("Handbook of Inorganic Chemistry"). Edited by Dr. R. ABEGG. Vol. II., Part II. Leipzig: S. Hirzel. 1905.

IS the second part of Vol. II. of this handbook the elements of the second group of the periodic system are treated. The theoretical aspects of the chemistry of these elements is emphasised, great stress being laid upon the results of investigations from a physico-chemical point of view. For each element a compendious bibliography is given, and special articles on the atomic weights have been prepared by Professor Brauner, the values having been very carefully re-calculated for the purpose. Spectral phenomena are only lightly touched upon, the full discussion of spectrum analysis being relegated to the ninth and general volume, and some inorganic compounds of only limited interest have been excluded, though the most important and characteristic organic salts, such as formates, acetates, &c., and the organo-metallic bodies, are regarded as coming within the sphere of the book. The need of an authoritative text-book of pure chemistry of the nature of this treatise has undoubtedly been felt, and this need seems likely to be admirably supplied by Dr. Abegg's book.

La Théorie Moderne des Phénomènes Physiques Radio-activité, Ions, Electrons. ("Modern Theory of Physical Phenomena, Radio-activity, Ions, Electrons"). By AUGUSTO RIGHI. Translated by EUGENE NÉCULCÉA. Paris: L'Éclairage Électrique. 1906.

THE French translation of Prof. Righi's interesting book has been prepared from the second Italian edition. An English version of the same book was noticed in these columns a short time ago, and little remains to be added to the comments then expressed. The translator has provided some explanatory notes, especially on the subject of radio-activity, giving fuller details of the phenomenon of scintillation, of induced radio-activity, and of the heat evolved by a radium salt, &c., and Prof. Lippmann has written a short introduction to the book, in which we notice a curious mistranslation in a quotation from the original relating to the supposed elastic deformations of the ether; otherwise the translation has been accurately and carefully performed, and the book should appeal to a large circle of readers in France.

Physikalische Krystallographie. ("Physical Crystallography"). By P. GROTH. Fourth Edition. Leipzig: Wilhelm Engelmann. 1905.

ALTHOUGH the author of this work speaks of it in the preface as an elementary text-book of crystallography, the fourth edition can lay claim to being one of the most complete treatises on the subject which has yet been written, containing accounts of all the most recent researches. The book is now divided into three sections; the first enumerates and discusses the properties of crystals in general, while in the second a systematic description of the various classes of crystals is given with numerous examples. The last section deals with methods of investigating crystals, th

calculation and graphic representation of crystal forms, the measurement of angles and refractive indices, and their optical examination in polarised light. In the short section on the apparatus for the determination of hardness and elasticity of crystalline substances, only the simplest instruments are described and those most suited for the use of beginners. The book is fully illustrated throughout, and the author has overlooked no important advance in our knowledge of the science, while his compendious work throws considerable light upon the question of the correlation of composition and crystalline forms.

Traité de la Fabrication de la Soude d'Après le Procédé à l'Ammoniacque. ("Treatise on the Manufacture of Soda by the Ammonia Process"). By H. SCHREIB. Translated from the German by Dr. L. GAUTIER. Paris and Liège: Ch. Béranger. 1906.

THE author of this work has had great experience of the working of the ammonia process for the manufacture of soda, and is well qualified to report upon it, and in the absence of a book devoted exclusively to the consideration of the method, the translation of it will undoubtedly be welcomed by French-speaking chemists and manufacturers. The book describes fully the various modifications of the process, appraising the practical value of each, and gives many plans and illustrations, so that the increasing number of those who are giving up the practice of the Leblanc method and are interested in the installation of new factories will find it a valuable aid in their work, while the chemists and managers of ammonia-soda factories may be strongly advised to add it to their libraries.

CORRESPONDENCE

ACTION OF LIGHT ON GLASS.

To the Editor of the Chemical News.

SIR,—In the course of an article which appeared in the CHEMICAL NEWS (vol. xci., p. 192) on the "Action of Ultra-violet Light upon Glass containing Manganese," I notice a remark upon the violet colouration produced upon such glass by the action of sunlight at the high altitude of Uyuni in Bolivia.

It may be of interest to note that in this district (Northern Chile) the same effect readily takes place at the sea-level. A fragment of common table-glass shows a decided violet tinge after less than a month of exposure to the sun. In the various specimens which I have examined, manganese has been present.—I am, &c.,

OSWALD H. EVANS, F.G.S.

Taltal, Chile.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 25, December 18, 1905.

At the annual Meeting of the Academy of Sciences, reports of the work of the various prizewinners were read and adopted. Among others, prizes were awarded as follows:—

Prix Zeecker to MM. Sabatier and Senderens—"On the Catalytic Effects of a certain number of Metals."

Prix Cahours to MM. Binet du Jassoneix and Kling.

Prix La Caze to Albert Colson for his researches in organic, mineral, physical, and industrial chemistry.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 16, 1905.

Quantitative Determination of Bismuth, and its Separation from Copper, Cadmium, Mercury, and Silver.—Arthur Staehler and Wilhelm Scharfenberg.—Bismuth cannot be determined as Bi_2O_3 in presence of hydrochloric or sulphuric acid, as basic salt is precipitated. The determination as sulphide gives results which are always too high, because the sulphide retains sulphur, and is, moreover, very easily oxidised. Better results are obtained by Rose's method of fusing the sulphide with potassium cyanide, and thus converting into metal. The precipitation of the phosphate or arsenate of bismuth seems to be the most generally applicable method, and the most satisfactory. The authors have found that the biphosphate of bismuth is quite insoluble in phosphoric acid solution, and they can thus separate bismuth from many other metals, *e.g.*, copper, cadmium, silver, and mercury, whose phosphates are soluble in phosphoric acid. Bismuth can be separated quantitatively by means of sodium phosphate in acid solution, without the reaction being affected by the presence of chlorides or by the strength of the nitric acid used. A 10 per cent solution of trisodium phosphate was used, and a bismuth solution prepared by dissolving pure bismuth in strong nitric acid. This bismuth solution was diluted with water and boiled, any precipitate of basic salt being removed by the addition of a little nitric acid. The boiling sodium phosphate solution was then added drop by drop to it, stirring gently all the time. The whole was boiled for a short time, and then the precipitate settled readily. It was filtered off hot, and washed with 1 per cent nitric acid containing a trace of ammonium nitrate, the filtrate always being tested for bismuth. The precipitate was dried at 120° in a Gooch's crucible, ignited over a Bunsen burner for five to ten minutes, and weighed as BiPO_4 . To separate bismuth and cadmium, the bismuth is first precipitated as above, and then, in absence of hydrochloric acid, the cadmium is separated electrolytically from ammoniacal solution to which some potassium cyanide has been added. In presence of hydrochloric acid the cadmium is separated as CdS , by passing sulphuretted hydrogen into the filtrate from the bismuth. The sulphide is then dissolved in nitric acid and electrolysed, after the addition of caustic potash and potassium cyanide. Mercury is quickly and accurately separated from hot ammoniacal solution as sulphide, quite free from excess of sulphur, after the bismuth has been precipitated as phosphate. Lead phosphate is separated quantitatively from neutral solution by means of sodium phosphate. However, the microscopic examination of the precipitate shows that it consists of at least three different phosphates, which by prolonged boiling are converted into tertiary lead phosphate. This behaviour indicates the way to separate lead and bismuth in presence of hydrochloric acid. Both phosphates are first precipitated with sodium phosphate, and the lead is then removed by boiling with 1 per cent nitric acid. A second method, which would undoubtedly be successful, is to heat to 500° a mixture of bismuth oxychloride and lead chloride in a current of sulphur monochloride and chlorine. At 447° the bismuth goes over as chloride, while the lead chloride remains behind.

Palladium.—A. Guthier and A. Krell.—Alkylated anilines and their haloid hydrates exhibit a characteristic behaviour towards palladous haloids. When a small quantity of chlor- or brom-hydrate of the base employed acts upon excess of palladous chloride or bromide, double salts result, and on reversing the reaction the palladosamine derivatives are obtained, which is not the case if the aromatic amines are alkylated in the side chain. In this case the tendency to form double salts is greatly increased, and crystalline products are obtained, both from dilute alcohol and from the corresponding dilute haloid acid, in whatever order the reagents are added, and also when the free base or an alcoholic solution of it acts upon the palladous haloid. The corresponding palladosamine de-

rivatives are obtained:—(1) By the action of an alcoholic solution of the corresponding base upon neutral aqueous solutions of chloro- or bromo-palladites; (2) by heating aqueous solutions of the double salts freed from excess of acid; (3) by allowing small quantities of the palladous haloid solution to act upon an excess of the base dissolved in alcohol. These derivatives of palladosamine are characterised by their light colour and by the fact that they are difficultly soluble, although they crystallise very well from large quantities of dilute alcohol. They dissolve easily in warm concentrated ammonia, and are then converted into palladosamine chloride or bromide, ammonia taking the place of the organic base.

Action of Bromine upon Trimethylamine.—James F. Norris.—By the action of bromine on trimethylamine a compound is obtained to which the author ascribes the formula $(\text{CH}_3)_3\text{NHBBr}$. To confirm this formula the author brings forward the following facts:—(1). The substance is formed by the action of bromine upon trimethylaminebromhydrate, $(\text{CH}_3)_3\text{N} \cdot \text{HBr} + \text{Br} = (\text{CH}_3)_3\text{NHBBr}$; (2) as it seemed possible that this reaction might proceed as follows: $(\text{CH}_3)_3\text{NHBBr} + \text{Br}_2 - (\text{CH}_3)_3\text{NBr}_2 + \text{HBr}$, and lead to the formation of a bromine addition product, a careful investigation was performed to ascertain whether hydrobromic acid was split off, but the result was negative; (3) hence it was to be concluded that the hydrobromic acid necessary for the formation of $(\text{CH}_3)_3\text{NHBBr}$ from trimethylamine and bromine resulted in a secondary reaction in which a part of the amine was decomposed by the halogen, hydrobromic acid being formed; (4) analysis showed that the total amount of bromine in the substance corresponded to the formula $(\text{CH}_3)_3\text{NHBBr}$. On addition of water and potassium iodide exactly half the bromine present was set free.

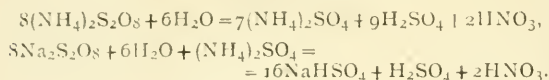
Determination of Nitrous Acid.—F. Raschig.—The author has investigated the determination of nitrous acid, using the method described by Meisenheimer and Heim (*Berichte*, 1905, xxxviii., 3834; *CHEMICAL NEWS*, 1905, xcii., 304); however, he does not measure the nitric oxide, but prefers to determine the iodine separated by titration with thiosulphate, which is naturally much quicker than measuring the gas. This method is useful only when the far more convenient permanganate oxidation method cannot be employed. Lunge added the nitrite solution very slowly to a known quantity of acid, $\frac{1}{2}\text{N}$. permanganate solution, warmed to 40°C . This method has the disadvantage that the errors in the determination are the greater the stronger the nitrite is, and, moreover, the decoloration of the permanganate proceeds so slowly towards the end that it is very easy to add too much nitrite, and this error cannot be rectified by a back titration. Moreover, sometimes manganese peroxide separates and cannot be removed by fresh additions of nitrous solution. All these drawbacks are avoided by the author's method. He uses an excess of about 20 per cent of permanganate. If necessary acid is added (this is of course superfluous in the case of nitroso acids), and after two minutes all nitrous acid is oxidised to nitric. Then the excess of permanganate is determined, the best process being that of Volhard, in which potassium iodide is added, and the iodine set free is titrated with thiosulphate.

Quantitative Determination of Bismuth and its Separation from the Heavy Metals as Phosphoric Acid Salt.—H. Salkowski.—The author recommends the precipitation of bismuth as phosphate, if the precipitation liquid contains no hydrochloric acid or chloride; the only free acid which may be present is nitric acid. He has obtained satisfactory results in separating bismuth from copper and also from lead. The almost complete insolubility of bismuth phosphate in dilute nitric acid provides a convenient test for showing the presence of bismuth qualitatively.

Oxidations with Silver Peroxide. I. Oxidation of Oxalic Acid.—R. Kempf.—A very large number of

organic substances at the ordinary temperature immediately take away the brown colour of a mixture of a solution of potassium persulphate with a silver nitrate solution, an oxidation process taking place. As the silver peroxide is regenerated, so long as persulphate is present a very small quantity of the silver salt suffices to cause all the persulphate to react. If a solution of oxalic acid is added to a solution of sodium or ammonium persulphate in dilute sulphuric acid no reaction occurs, but as soon as small quantities of a silver salt are added a violent reaction takes place, accompanied by spontaneous warming and frothing. The oxalic acid is quantitatively oxidised to carbon dioxide. This process may be used to estimate volumetrically the active oxygen in persulphates, an excess of oxalic acid being used and titrated back with potassium permanganate solution, and the process is found to be more reliable and accurate than any other.

Oxidations with Silver Peroxide. II. Formation of Nitric Acid from Ammonium Sulphate.—R. Kempf. —When silver sulphate is added to a solution of ammonium persulphate in dilute sulphuric acid, the brown colour which first appears always vanishes after some days, although no oxygen is evolved, nor is any persulphuric acid still present in the liquid. Considerable quantities of nitric acid are to be found in the liquid, and its formation provides an explanation of the phenomena observed. The nitric acid can only be formed by the oxidation of the ammonium salt at the ordinary temperature in acid solution by means of silver peroxide. The author has found that sodium persulphate similarly converts zinc ammonium sulphate into nitric acid, the yield being almost quantitative in all cases, so that neither nitric acid nor free nitrogen can result to an appreciable extent. The reaction occurs according to the following equations:—



The velocity of the reaction is very small. In absence of a silver salt a persulphate solution cannot oxidise combined ammonia in sulphuric acid solution to nitric acid, and thus the energetic oxidation action is due only to the silver peroxide and not to the persulphuric acid or its products—ozone (which is formed in large quantities when a solution of persulphate in sulphuric acid is warmed), Caro's acid, or hydrogen peroxide. In the experiments above described the ammonium salt was present in great excess; if excess of persulphate is used, only about 69 per cent. of the ammonium present is converted into nitric acid. The general results of the author's work on the oxidation of ammonium salts to nitric acid may be summarised as follows:—1. Alkali persulphate oxidises ammonium salts in sulphuric acid solution in presence of silver sulphate almost quantitatively to nitric acid at the ordinary temperature. 2. In the absence of silver salts this oxidation does not take place. 3. In alkaline solution alkali persulphate oxidises free ammonia to nitric acid at the ordinary temperature without any catalyst. 4. (According to Marshall), in ammoniacal solution alkali persulphate oxidises ammonia in presence of silver sulphate only to elementary nitrogen.

Vanadium Sesquisulphates.—Arthur Stahler and Heinz Wirthwein. —Using the same method as that adopted for the preparation of titanium sulphuric acid (*Berichte*, 1905, xxxviii., 2620), the authors have prepared a complex vanadium sesquisulphate sulphuric acid of the composition $\text{V}_3(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 + 12\text{H}_2\text{O}$. From this acid two coloured salts could be prepared, viz., the ammonium and rubidium salts. When gently heated the acid gives up water and sulphuric acid, and yields yellow anhydrous vanadium sesquisulphate. This, like the corresponding sesquisulphates of iron, chromium, and titanium, is insoluble in water and sulphuric acid. When the vanadium sesquisulphate sulphuric acid is heated to a higher temperature, vanadium pentoxide is formed.

MISCELLANEOUS.

The Iron and Steel Institute.—*The Andrew Carnegie Research Scholarship.*—A Research Scholarship or Scholarships, of such value as may appear expedient to the Council of the Iron and Steel Institute from time to time, founded by Mr. Andrew Carnegie (Past-President), who has presented to the Iron and Steel Institute eighty-nine one-thousand dollar 5 per cent Debenture Bonds for the purpose, will be awarded annually, irrespective of sex or nationality, on the recommendation of the Council of the Institute. Candidates, who must be under thirty-five years of age, must apply on a special form before the end of February to the Secretary of the Institute. The object of this scheme of Scholarships is not to facilitate ordinary collegiate studies, but to enable students, who have passed through a college curriculum or have been trained in industrial establishments, to conduct researches in metallurgy of iron and steel and allied subjects, with the view of aiding its advance or its application to industry. There is no restriction as to the place of research which may be selected, whether university, technical school, or works, provided it be properly equipped for the prosecution of metallurgical investigations. The appointment to a Scholarship will be for one year, but the Council may at their discretion renew the Scholarship for a further period instead of proceeding to a new election. The results of the research shall be communicated to the Iron and Steel Institute in the form of a paper to be submitted to the Annual General Meeting of members, and if the Council consider the paper to be of sufficient merit, the Andrew Carnegie Gold Medal shall be awarded to its author. Should the paper in any year not be of sufficient merit, the Medal will not be awarded in that year.

Association of Teachers in Technical Institutes.—The following is a copy of a memorandum relating to the syllabus of instruction in practical organic chemistry which has been approved by the Council of the above Association, and forwarded to the Secretary of the Board of Education:—

Memorandum.—The Council of the Association of Teachers in Technical Institutions desire to draw the attention of the Board of Education to the following proposals regarding the syllabuses of certain science subjects, and respectfully request that the proposals shall be placed before the examiners and others concerned with these subjects with the view of modification in the directions indicated, and thereby it is believed materially improving the teaching of the said subjects.

Practical Organic Chemistry.—It is generally felt that the syllabus in its present form is most unsatisfactory, inasmuch as too great prominence is given to qualitative analysis, i.e., the detection in a mixture of two organic constituents from a given list. Whilst fully recognising that the student should be able to identify the more important organic compounds, we submit that the training necessary to enable him to analyse mixtures of the type set, is not such as really deepens his knowledge of the essential properties of the substance dealt with, since the majority of the tests and methods of separation applicable to such mixtures do not involve the fundamental characteristics of the compound nor the principal methods of organic chemistry. At present students have to curtail seriously the time which should be given to organic preparation, and devote their energies to the detection of the constituents of such mixtures as, for instance, potassium, cyanide, and cane-sugar, urea, and starch. We suggest that the object of the practical organic chemistry should be primarily the study of the reactions characteristic of the various classes of organic substances, emphasising as far as possible their applicability to a whole class, and not merely to individual compounds, with elementary analysis, the determination of certain physical constants and molecular weights in addition. The syllabus would, therefore,

read somewhat as follows:—Stage I (Aliphatic). Elementary qualitative analysis, determination of melting points and boiling points, reference of compounds to their classes, and preparation of derivatives; preparation and identification of a few typical compounds. Stage II. (Aromatic). Similar to Stage I. Stage III. Elementary quantitative analysis and determination of molecular weights. Preparation and detection of typical organic compounds.—I remain, on behalf of the Council, yours truly, J. WILSON, Hon. Secretary.

Two Iodo-mercurates of Lithium.—A. Duboin.—The author obtained long fine needles of $2LiI, HgI_2, 6H_2O$ by leaving a saturated solution of mercuric iodide and lithium to stand during August, September, and October. He gives the full analysis of the compound, and describes the needles as flattened and striated along their length and very deliquescent. The density at 0° is 3.26 . They are decomposed by water and are soluble in several alcohols, glycerin, aldehyde, acetone, and many other organic liquids. They are less soluble in nitrobenzene; insoluble in benzene and methyl iodide. **Second Iodo-mercurate.**—On cooling the above mother-liquor at 8° large crystals were found floating on the surface in the shape of small prisms. The analysis corresponded to the formula $2LiI, HgI_2, 8H_2O$. The density was 2.95 , and in other respects the crystals behaved as those of the preceding compound.—*Comptes Rendus*, cxli., No. 24.

A New Compound: Fluoride of Bromine, BrF_3 .—Paul Lebeau.—The author has isolated this compound (the existence of which has been recognised by M. Moissan), obtained by the action of fluorine on bromine, in a special set of apparatus consisting of glass and platinum. The composition of the compound was established by a study of its action on water and alkaline solutions. It is a colourless liquid, fuming in the air and giving off very irritating vapours. Its point of fusion lies between 4° and 5° . In the solid state it consists of a mass of beautiful colourless prisms. The chemical activity is great; a crystal of iodine thrown on to the surface of solid fluoride cooled below -10° leaves a yellow stain, then brown, and as the temperature rises the action becomes more vigorous, and the pentafluoride of iodine of M. Moissan and vapour of bromine are formed with incandescence. Sulphur in contact with the solid fluoride is inactive, but on melting it burns and gives a mixture of fluoride and bromide of sulphur. Red phosphorus, arsenic, antimony, boron, silicon react in the cold, while with carbon it has to be heated gently to start the reaction. It reacts with most of the metals and on many of their compounds. With organic compounds it behaves like fluorine. **Conclusions.**—Fluorine and bromine combine directly, giving a compound BrF_3 , a liquid which is colourless and giving a fusible solid at 4° ; it behaves chemically like fluorine.—*Comptes Rendus*, cxli., No. 24.

MEETINGS FOR THE WEEK.

TUESDAY, 23rd.—Royal Institution, 5. "Impressions of Travel in China and the Far East," by Prof. Edward H. Parker, M.A.

WEDNESDAY, 24th.—Society of Arts, 8. "The Planting of Waste Lands for Profit," by Dr. J. Nisbet.

THURSDAY, 25th.—Royal Institution, 5. "Shakespeare," by the Rev. Canon Henry Charles Beeching, M.A., &c. Society of Arts, 8. (Howard Lectures). "High Speed Electrical Machinery, with special reference to Steam Turbine Machines," by Prof. Silvanus Thompson, F.R.S.

FRIDAY, 26th.—Royal Institution, 9. "Walter Pater," by Arthur C. Benson, M.A.

SATURDAY, 27th.—Royal Institution, 3. "The Church in France," by J. E. C. Bodley.

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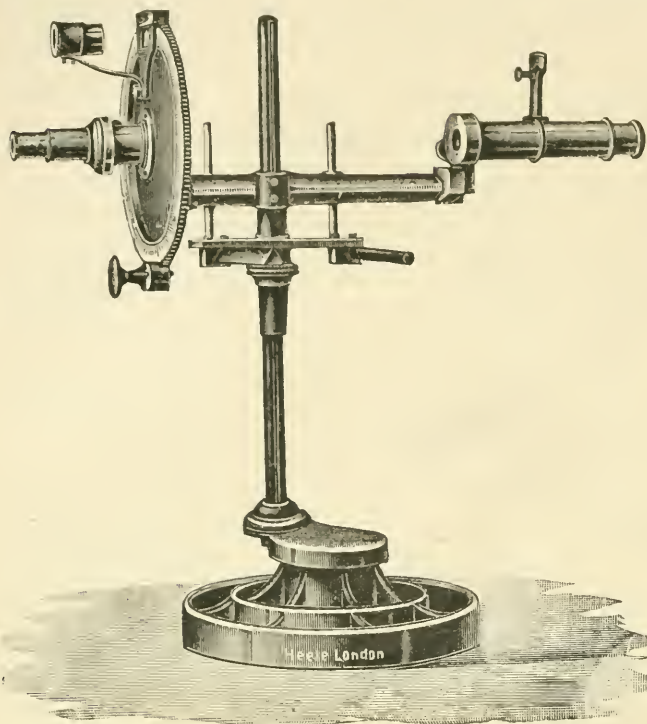
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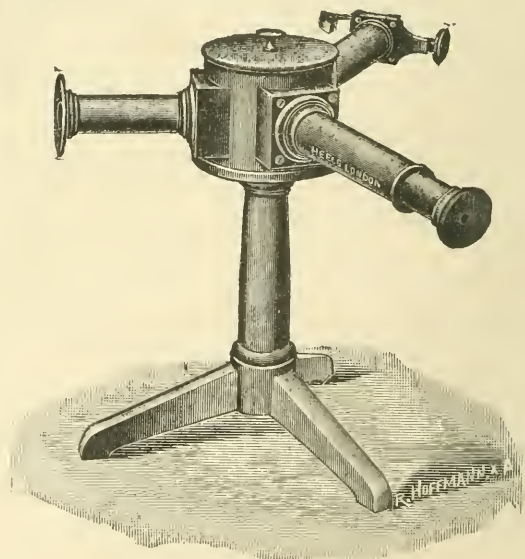
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THE CHEMICAL NEWS.

VOL. XCIII., No. 2409.

NEW RESEARCHES ON THE ATOMIC WEIGHT OF NITROGEN.*

By PHILIPPE A. GUYE.

(Concluded from p. 23).

THE lowering of the atomic weight of silver is now made manifest by a new cycle of calculations, of which it is advisable to indicate the principle and the primary applications.

When the value of an atomic weight is to be fixed, a gravimetric ratio between the atomic weight sought and an atomic weight supposed known is made use of. For the latter, one of the atomic weights of Stas' cycle is generally taken, without any regard to the accuracy of such a weight.

The latter being based on oxygen by three atomic ratios (except silver, which is by two), it is forgotten that their accuracy cannot exceed $\pm 3/10000$ of their value ($2/10000$ for silver), and that the atomic weight sought, which results from a fourth gravimetric ratio, is only correct to $4/10000$, *i.e.*, to $1/2500$; nevertheless, the majority of experimenters calculate, for example, atomic weights such as those of gold (206.960), mercury (200.045), platinum (194.917), &c., to three decimal places, as if correct to $\pm 1/200000$!

Thanks to physico-chemical methods, a process of calculation can to-day be evolved much more logical and more accurate, which consists in only considering as accurately known the atomic weights determined, on the one hand, by physico-chemical methods, and on the other by gravimetric ratios referred directly to oxygen.

Actually three atomic weights satisfy this double condition, those of hydrogen, carbon, and nitrogen, of which the values are—

$$C = 12.002, N = 14.009, H = 1.0076,$$

accurate to $1/10000$, approximately.

It is to be hoped that the subsidiary work will rapidly increase the number, and that soon the elements S, Cl, P will be added to this list.

However that may be, we can start from the above three elements; from them we can revise the gravimetric ratios formerly determined to refer the elements C, N, H to silver, using them to resolve the inverse problem, that is to fix the atomic weight of silver.

The numerical values of those gravimetric ratios have been carefully calculated by Clarke ("Re-calculation of the Atomic Weights, 1897, Washington"), treating the experimental data of different experimenters by the method of the least squares.

For a first application we may be content with these values.

With these data, the following ratios are obtained:—

I. Ratio Ag : AgNO₃.

According to the experiments of Penny, Marignac, Stas, and Hardin (30 determinations),—

$$100 \text{ p Ag} = 157.479 \text{ p AgNO}_3.$$

Putting NO₃ = 62.009, we have—

$$\text{Ag} = 100 \times \frac{62.009}{57.479} = 107.882.$$

II. Ratio Ag : CH₃COOAg (Silver Acetate).

According to the experiments of Liebig and Redtenbacher, Marignac, and Hardin (20 determinations),—

$$100 \text{ p CH}_3\text{CO}_2\text{Ag} = 64.636 \text{ p Ag}.$$

Putting CH₃.CO₂ = 59.027, we have—

$$\text{Ag} = 59.027 \times \frac{64.636}{35.364} = 107.886.$$

III. Ratio Ag : C₇H₅O₂Ag (Silver Benzoate).

According to Hardin's 10 determinations,—

$$100 \text{ p C}_7\text{H}_5\text{O}_2\text{Ag} = 47.125 \text{ p Ag}.$$

Putting C₇H₅O₂ = 121.052, we have—

$$\text{Ag} = 121.052 \times \frac{47.125}{52.875} = 107.888.$$

Recapitulating, we have:—

TABLE XVI.

Ratio	Ag : AgNO ₃	Atomic weight, Ag
"	Ag : CH ₃ CO ₂ Ag	107.882
"	Ag : C ₇ H ₅ O ₂ Ag	107.886
		107.888
Mean		107.885

This result calls for certain remarks.

In the first place, it will be recognised that three independent methods to fix one atomic weight have rarely—perhaps never—given such a degree of agreement. The extreme divergence is scarcely $6/100000$, whilst between the different determinations of Stas this difference is of the order $1/5000$. Besides, it would have sufficed to take C = 12.001 instead of C = 12.002 in order to reduce the above numbers to 107.882, 107.883, 107.882.

In the second place, it is to be noticed that the first ratio is almost a direct ratio to oxygen, the group NO₃, supposed known, containing about 76 per cent of this element. Further, the extreme divergence of the different values obtained for the atomic weight of nitrogen is ± 0.005 with reference to the mean 14.009, *i.e.*, less than $1/10000$, referring it to the weight of the group NO₃ = 62.009. From this fact the atomic weight Ag = 107.882 is correct to $\pm 1/10000$. Attributing, finally, as before, a precision of $\pm 1/10000$ to the gravimetric ratio Ag : AgNO₃, we conclude that the atomic weight Ag = 107.882 is correct to $\pm 2/10000$ in the case in which the errors add together. In other words, the atomic weight of silver cannot, in any case, exceed 107.90, nor be less than 107.86.

If, finally, one compares the mean 107.885 with the generally admitted value 107.93, the divergence is 0.055, *i.e.*, about $1/2000$. This result is full of meaning, for a very large number of atomic weights are determined with reference to silver; if it is confirmed, the present table of atomic weights will have to be almost completely revised. I admit that it is with some hesitation that I venture to formulate this conclusion. It is so unexpected that it seems good to add some formal reservations, until a deeper investigation of the question has been accomplished.

In order to give a more complete idea of the new cycle of calculation to apply to the atomic weight of silver, it is useful to indicate, but with many more reservations, the values to which lead the incompletely controlled physico-chemical atomic weights of the elements Cl, S, P.

Their values, as calculated by various physico-chemical methods, are:—

	Cl.	S.	P.
Leduc	35.470	32.056	30.975
D. Berthelot	35.479	32.058	30.978
Guye	35.476	32.065	30.978
Mean	35.475	32.060	30.977

I would repeat that these numbers are far from affording the same scientific value as those obtained for O, H, and

* From the Bulletin de la Société Chimique de Paris, 1905.

N. Each of them has been merely furnished from observations relative to a single gas, the densities of the compounds SO_2 , HCl , PH_3 ; one of these densities only (SO_3) has been checked by two observers; finally, we possess for none of the elements S, P, Cl the gravimetric control of a good ratio to oxygen. Here, therefore, there are important depths to fathom by independent researches, which will be able to modify more or less the above means.

With these reservations, we now give the values of the atomic weight of silver obtained from these means, using, as before, the values of the gravimetric ratios re-calculated by Clarke.

IV. Ratio Ag : NH_4Cl .

According to the experiments of Pelouze, Marignac, and Stas (26 determinations).—

$$100 \text{ p Ag} = 49.598 \text{ p NH}_4\text{Cl}.$$

Putting $\text{NH}_4\text{Cl} = 53.511$, we have—

$$\text{Ag} = 100 \times \frac{53.514}{49.598} = 107.895.$$

V. Ratio of Chlorine to Silver Ag : Cl.

According to the latest determinations of Richards, already quoted (10 determinations).—

$$100 \text{ p Ag} = 32.867 \text{ p Cl}.$$

Putting $\text{Cl} = 37.475$, we have—

$$\text{Ag} = 100 \times \frac{35.475}{32.867} = 107.932.$$

VI. Ratio Ag_2 : Ag_2S .

According to the experiments of Dumas, Stas, and Cooke (17 determinations).—

$$100 \text{ p Ag} = 114.858 \text{ p Ag}_2\text{S}.$$

Putting $\text{S} = 32.060$, we have—

$$\text{Ag} = 100 \times \frac{32.060}{14.858} = 107.884.$$

VII. Ratio Ag_2 : Ag_2SO_4 .

According to the experiments of Struve and Stas (12 determinations).—

$$100 \text{ p Ag}_2\text{SO}_4 = 69.205 \text{ p Ag}.$$

Putting $\text{SO}_4 = 96.060$, we have—

$$\text{Ag} = \frac{96.060}{2} \times \frac{69.205}{30.795} = 107.928.$$

VIII. Ratio Ag_3 : PO_4Ag_3 .

According to 2 determinations of Van der Plaats, on 1 grm. of silver phosphate.—

$$100 \text{ p PO}_4\text{Ag}_3 = 77.313 \text{ p Ag}.$$

Putting $\text{PO}_4 = 94.977$, we have,—

$$\text{Ag} = \frac{94.977}{3} \times \frac{77.313}{22.687} = 107.888.$$

Recapitulating the values given by the Ratios IV. to VIII., we have:—

TABLE XVII.

Ratio	Ag		Ag.
Ag : NH_4Cl	..	..	107.895
Ag : Cl	..	..	107.932
Ag_2 : Ag_2S	..	..	107.884
Ag_2 : Ag_2SO_4	..	..	107.928
Ag : PO_4Ag_3	..	..	107.888

Mean 107.905

This mean only differs from the preceding one by 2 10000.

Although the values of this second series are less in agreement than those of the first, for the reasons given above, the extreme values 107.932 and 107.888 only differ among themselves by 0.044; they agree among themselves

more than the extreme values of the means calculated by Clarke, 107.907 and 108.194 (for a total of seven means, the mean of which is 107.924), thus presenting a divergence of 0.287, which is six times greater than the preceding.

Combining the two means 107.885 and 107.905, with a double weight for the first, we get to the final value—

$$\text{Ag} = 107.892,$$

or, in round numbers,—

$$\text{Ag} = 107.89 \text{ or } \text{Ag} = 107.9.$$

which represents the probable atomic weight of silver deduced from the system of atomic weights C, N, H, Cl, S, P, to which we have been led.

I shall return later to this question. The preceding exposition will suffice to make manifest the interest attaching to a revision of the atomic weights according to a new principle consisting of a combination of physico-chemical and gravimetric results.

The first application of this principle, of which I have just submitted the results, certainly shows that a new and fruitful path is opening before us. It will allow of using in a much more rational manner the valuable materials accumulated for nearly a century by all the scientists who have undertaken the determination of gravimetric atomic ratios. I have a secret hope that this work, and that of Stas in particular, may finally appear much more accurate than to-day.

P.S.—Since the assembling of this Conference certain new observations give further precision to the preceding conclusions. I will summarise them in a few words.

1. The experiments executed in my laboratory, in co-operation with Davila, confirm to a few ten-thousandths the value of the density of nitrogen dioxide found by Gray; these experiments, in process of completion, will be published shortly.

2. The critical constants of ammonia gas have been revised in my laboratory by A. Jaquerod.

Applying the method by reduction of the critical elements to the weight of a normal litre of this gas, as determined by Pintza and myself, the molecular weight of NH_3 is found to be—

$$M = 17.035.$$

whence—

$$N = 17.035 - 3.023 = 14.012,$$

a value which is within the limits previously found by physico-chemical methods.

3. Dixon and Edgar have just determined the atomic weight of chlorine by the ratio Cl : H, and have found (for H = 1.0076 or O = 16) Cl = 35.463, a result from which it is to be concluded that the density of the gas HCl , determined by Leduc, is probably a little high, and ought consequently to be revised.

Calculating provisionally with this value, Cl = 35.463, the atomic ratios iv. and v., which give the atomic weight of silver, Table XVII. ought to be revised as follows:—

Methods.	Ag.
Ratio Ag : NH_4Cl	107.871
Ag : Cl	107.895
Ag_2 : Ag_2S	107.884
Ag_2 : Ag_2SO_4	107.928
Ag_3 : Ag_3PO_4	107.888

The mean is 107.892. If the value furnished by the ratio Ag_2 : Ag_2SO_4 be excluded, the mean is—

$$\text{Ag} = 107.886,$$

which is identical with that furnished by the more exact ratios of Table XVI., i.e.,—

$$\text{Ag} = 107.885.$$

The atomic weight of silver, obtained by starting with the elements C, H, N, Cl, S, P, from the mean of seven independent atomic ratios, is therefore contained between

107·871 and 107·895. Its exact value apparently ought not to exceed—

$$Ag = 107·89.$$

From this is evident the desirability of establishing definite and concordant values of the atomic weights of Cl, S, P by physico-chemical and gravimetric methods.

4. The lowering of the atomic weight of silver will involve the lowering of a great number of atomic weights. It would be premature to express an opinion as to the number, but it is already obvious that the result will be to increase greatly the agreement of the gravimetric ratios. I will quote as an example the ratio NaCl: NaNO₃. With Ag=107·885, Cl=35·463, N=14·009, and Na=22·998 (Richards' recent value Na=23·008 for Ag=107·93, reduced to Ag=107·885), we calculate—

$$100 \text{ NaCl} = 145·408 \text{ NaNO}_3,$$

whilst the mean deduced by Clarke from 23 determinations by Penny, Stas, and Hibbs give—

$$100 \text{ NaCl} = 145·418 \text{ NaNO}_3.$$

At 1/15000 about, the limit of accuracy of the experiments, the two values agree.

This is a confirmation of the new value of the atomic weight of silver, which is the subject of the preceding considerations.

THE THERMO-CHEMICAL RELATIONS OF CARBON, HYDROGEN, AND OXYGEN.

By JOHN CLARK THOMLINSON, B.Sc. (Dunelm).

A CONSIDERATION of the thermo-chemical data available to the physical-chemist has led to the following results in an attempt to determine the heats of combination of the elements carbon, hydrogen, and oxygen.

The formation of methane, CH₄, and ethane, C₂H₆, takes place with the evolution of 21·750 calories and 28·560 calories respectively, and assuming that the heat of combination of carbon and hydrogen is the same in both reactions we obtain as a result C = -8·130 calories, H = 7·470 calories, carbon having a negative value corresponding to an actual absorption of heat during reaction.

To confirm the assumption we have just made, we find on applying these values to the higher hydrocarbon propane, C₃H₈, of this series that the calculated heat of formation is 3·537 calories, closely agreeing with the number 3·511 calories obtained by experiment.

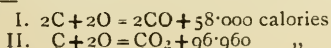
Hence we may say in the compounds under consideration that the mode of union of the carbon atoms in ethane and propane in no way affects the thermal value of that element.

Methane, ethane, and propane are, however, all saturated compounds; when we take into consideration the heats of formation of the corresponding unsaturated hydrocarbons, we find we have to assign a different value to the heat of combination of carbon in such groups as C=C, C≡C.

Ethylene, C₂H₄, is formed with the absorption of 2·710 calories; acetylene, C₂H₂, has a heat of formation = -48·170 calories. If hydrogen still retains its value 7·470 calories, then C≡ = -16·300 calories, the symbol C≡ indicating a carbon atom united by two bonds of union to another carbon atom, and similarly in acetylene C≡ = -31·560 calories.

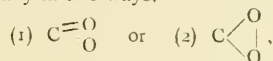
We have assumed here that hydrogen has the same heat of combination in unsaturated as in saturated hydrocarbons; the following thermo-chemical relations will support these conclusions:—

When carbon unites with oxygen to form carbonic oxide and carbon dioxide, a much greater evolution of heat takes place in the latter reaction, as is evident from the following equations:—



the heat of formation of one molecule of carbon dioxide being nearly double that of two molecules of carbonic oxide.

Further, the formula of carbon dioxide can be represented graphically in two ways,—



in which carbon is respectively quadri- and di-valent.

We should expect, as will be shown later is the case, that oxygen combining with both its bonds of union to another atom would cause a greater evolution of heat than the union of the group —O—O—, and are hence justified in regarding Formula 1, in which carbon is quadrivalent, as the true structural formula for carbon dioxide.

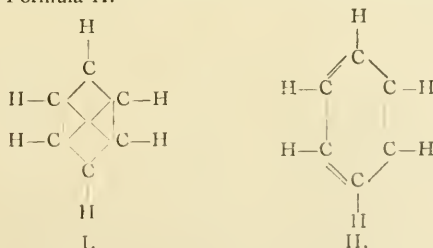
To return now to the formation of dioxide and monoxide, we find carbon quadrivalent in Equation II., whereas in Equation I. it is evidently divalent, and as the nature of the union of the oxygen in both compounds is the same, one quadrivalent carbon atom in uniting with two oxygen atoms gives rise to an evolution of 38·960 calories in excess of that due to two carbon atoms uniting with two atoms of oxygen to form two molecules of carbon monoxide, and since we have assigned to quadrivalent carbon a heat of combination -8·130 calories, that of di-valent carbon is -8·130 - 19·480 calories, i.e., is equal to -27·610 calories.

A comparison of these values for the heat of combination of carbon with those obtained for it in the case of ethylene and acetylene will show us that in these compounds carbon may be regarded as respectively tri- and di-valent.

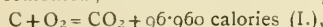
For quadrivalent carbon C≡ = -8·130 calories, and when di-valent carbon = -27·610 calories, the mean of these numbers representing tri-valent carbon if such exists as having a heat of combination = -17·870 calories, and the value obtained for the carbon atom in ethylene is C≡ = -16·300 calories.

Similarly, C≡ = -31·560 calories in acetylene and the value for divalent carbon as in carbonic oxide has been found to be 27·610 calories, giving as the experimental and calculated values (calculated from the latter value for divalent carbon), -48·170 calories and -40·280 calories respectively, which numbers although showing a difference of about 20 per cent is an approximation in favour of viewing carbon as having a di-valent value in acetylene.

In this connection it is interesting to note that in benzene, C₆H₆, the heat of formation, taking the ordinary number for the heat of combination of hydrogen H = 7·470 calories, gives a value for carbon C = -7·655 calories, so that this compound may be looked upon as being essentially a saturated hydrocarbon, in so far as its thermal value is concerned, corresponding to Formula I., which we should regard as more nearly indicating a condition of saturation than Formula II.



We see, then, that carbon must be looked upon as having different thermal values according to the manner in which it is combined; let us now return to Equation I.,—



which gives a value for the heat of combination of oxygen O=52·545 calories, with the ordinary value for quadrivalent carbon, which, with the numbers we have obtained for hydrogen, gives as the calculated heat of formation of water 67·485 calories.

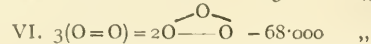
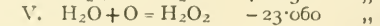
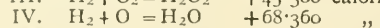
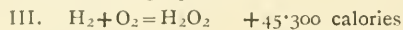
Now, water has been found experimentally to have a heat of formation 68·360 calories for the liquid and 59·133 calories for the gaseous product at 18—20° C.

We have hitherto been dealing with the latter conditions, and here the calculated and experimental values again show approximation, though truly not very closely, the difference being about 15 per cent.

We have, however, shown that we can obtain approximate values for the heats of combination of carbon, hydrogen, and oxygen, giving results for the heats of formation of compounds which show an agreement with those obtained by experiment that would lead to our assuming that such are approximately the conditions actually occurring during the formation of the compounds of these elements.

Further examples supporting those already given are those of hydrogen peroxide and ozone, which are formed from water and oxygen respectively with absorption of heat.

Compare the following equations:—



If $\text{H}-\text{O}-\text{O}-\text{H}$ be taken as graphic representation of the formula for hydrogen peroxide, we find the heat of combination of the group $-\text{O}-\text{O}-$ is equal to 30·360 calories, so that the entrance of a second atom of oxygen into the molecule of water would, according to the value we have already obtained for the heat of combination of an oxygen atom, $\text{O} = 52\cdot545$ calories, be accompanied by an absorption $52\cdot545 - 30\cdot360$ calories of 22·185 calories; that actually taking place as found by experiment is 23·060 calories.

Here we have the double bond of an oxygen atom in union with atoms of other elements broken up in such a way that one of the bonds becomes united with that of another atom of oxygen, this action having a thermal value = $-23\cdot060$ calories.

In the reaction represented by Equation VI. three molecules of oxygen are converted into two molecules of ozone, 68·000 calories being absorbed, and here the same action as in the case of hydrogen peroxide takes place, the splitting up of the double oxygen bond by union with a further atom of oxygen taking place in a threefold sense, and calculating from the value found in the case of hydrogen peroxide, we should expect a heat absorption equal to 69·180 calories; that actually taking place is 68·000 calories.

The heat of formation of amylene, C_5H_{10} , is 19·000 calories where the product is liquid; that obtained by calculation—and here, as in the following examples, the calculated values refer to gaseous products—is 17·710 calories.

Further examples are given in the following table:—

Compound.	Heat of formation determined experimentally.		Heat of formation by calculation.	
	Calories.		Calories.	
Acetic acid, $\text{C}_2\text{H}_4\text{O}_2$..	120	340	118	430
Propionic acid, $\text{C}_3\text{H}_6\text{O}_2$..	109	400	125	520
Oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$..	202	540	208	860
Cane-sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$..	601	500	644	775

In all these cases the numbers are greater when calculated than are found by experiment, in spite of the remarks made in the case of amylene, but considering what we have already found to be the nature of the union of carbon, hydrogen, and oxygen, we may find an explanation of this in the constitution of the compounds themselves.

Other examples might be quoted, but such thermo-chemical relations as we have hitherto studied may suffice to confirm us in considering certain values as at any rate approximately representing the heats of combination of the elements carbon, hydrogen, and oxygen.

This paper has been written with a view to bringing forward the thermo-chemical relations which have led to a

belief in such heats of combinations, and in such a branch of the science, where so many attendant phenomena, physical and otherwise, may affect the data we have to work with, what is only approximately true may be of value in elucidating the problems of thermo-chemistry.

THE CHEMICAL SEPARATION OF THE RADIO-ACTIVE TYPES OF MATTER IN THORIUM COMPOUNDS.*

By HERMAN SCHLUNDT and RICHARD B. MOORE.

(Concluded from p. 28).

The Theoretical Curves.

THE foregoing explanation for the initial peculiarities of the curves of recovery and decay finds further confirmation in the theoretical curves which are obtained on the basis of the suppositions made. The method of treatment here employed follows, in the main, the exposition given by Rutherford ("Radio-activity," 1904, pp. 268—272, 297—300) and by Stark ("Jahrbuch der Radioaktivität," 1904, i., 1). According to the disintegration theory, a constant proportion of the atoms of a radio-active element is continuously undergoing change, and the ionisation produced may be used for ascertaining the fraction of the atoms which are changing per second. This constant rate, called the *radio-active constant*, is the fundamental physical characteristic of the different radio-active types of matter. It has a different value for each type of active matter, but is a definite constant for each particular type. The radio-active constant for ThB is 0·0125, when the time is expressed in minutes, which indicates that ThB is continuously undergoing change at the rate of 1·25 per cent per minute. The ionisation produced by a particular type of radio-active matter depending, as it does, upon the number of atoms present and their rate of change, is directly proportional to the product of the rate and the number of atoms present. This law of radio-active change is the same as the law followed by a monomolecular chemical reaction, the inversion of cane-sugar for example, and both laws are illustrations of the more general law of nature which Lord Kelvin has happily termed the "Compound Interest Law," which states that the amount of change in a given time is directly proportional to the quantity present in the system (Mellor, "Higher Mathematics for Students of Chemistry and Physics," p. 40).

The rate of change of a radio-active element is expressed by the equation—

$$\frac{dn}{dt} = -rn;$$

where n denotes the number of atoms present at the time t , and r the radio-active constant, the minus sign indicating that the change causes a decrease in the quantity of the active element. By integration of the above equation,—

$$n = n_0 e^{-rt};$$

where n_0 denotes the number of atoms considered at the outset, when $t=0$. The activity, I , of the sample at the time t , is given by—

$$I = crn = crn_0 e^{-rt},$$

where c is the proportionality constant. The values of the theoretical curve of decay of ThX (Plate I.), were calculated from the above equation. The radio-active constant of ThX has the value 0·0072 when t is expressed in hours (Rutherford, "Radio-activity," p. 298).

When the radio-active substance produces another, which is also radio-active, then the activity at any time is proportional to the sum of the atoms of each which are undergoing change. The curve showing the progress toward equilibrium will then frequently show irregularities.

* From the *Journal of Physical Chemistry*, ix., No. 8, p. 682.

The residue obtained in the fumaric acid separation contains ThX and ThA just after separation, but ThA at once produces ThB, which changes rapidly into a final inactive product. The successive changes occurring simultaneously in the residue are:—

ThX $\Rightarrow$ Emanation $\Rightarrow$ ThA $\Rightarrow$ ThB $\Rightarrow$ Final Product.

The activity of the solid residue itself is due to ThX and ThB. In the consideration which follows, the second product, the emanation, is not introduced, since its rate of transformation is very rapid in comparison with the other products.

If n , n_1 , n_2 denote the number of atoms of ThX, ThA, and ThB present at the time t after separation, and r , r_1 , and r_2 the corresponding radio-active constants, then the activity I is expressed by

$$I = rn + k r_2 n_2 \dots \dots \dots (i),$$

where k denotes the ratio of the ionisation of ThB to ThX. The radio-active constants have the values, $r = 0.0072$; $r_1 = 0.063$; $r_2 = 0.75$, when t is expressed in hours. The value of n is obtained from the formula—

$$n = n_0 e^{-rt}.$$

The value of n_2 depends upon the value of n_1 , and is determined by the following considerations: Assuming that ThX and ThA are in equilibrium immediately after the separation, then the quantities of each present are inversely proportional to their radio-active constants; that is,—

$$n : n_1 = r_1 : r.$$

Introducing the values of r and r_1 we have—

$$n_1 = \frac{n}{8.75} = \frac{n_0}{8.75} e^{-rt}.$$

Now, the number of atoms of ThB continuously undergoing change is $r_2 n_2$, and the number produced from ThA at the same time is $r_1 n_1$. Hence the rate of change in ThB,—

$$\frac{dn_2}{dt} = -r_2 n_2 + r_1 n_1,$$

whence

$$\frac{dn_2}{dt} + r_2 n_2 = \frac{r_1 n_0}{8.75} e^{-rt}.$$

Integration of this equation gives—

$$n_2 = \frac{r_1 n_0}{8.75 (r_2 - r_1)} (e^{-rt} - e^{-r_2 t}).$$

The theoretical values in the following table were calculated from Formula 1. The value of $k = 0.5$ used, was obtained from the ratio of the ordinates of the activities of ThB and ThX at the end of the second day. The experimental values are given in the second and fourth columns of the table, whilst the first column gives the time which had elapsed since the separation. (See also Curves B and C, Plate I.).

Time.	Fumaric acid.	Theoretical value.	Pyridine.
0	100	100	100
20 minutes	—	111	—
30 "	116	115	108
60 "	129	127	113
2 hours	147	137	127
4 "	155	144	141
5 "	158	145	142
6 "	158	144	142
8 "	154	142	140
16 "	—	134	—
24 "	128	127	122
2 days	106	107	103
4 "	74	75	73
8 "	37	38	36
12 "	18	19	17
16 "	—	9.5	—
20 "	5.6	4.7	4.5

The times at which the theoretical and experimental values attain a maximum are practically the same, thus confirming the assumptions made. The variations of the experimental from the theoretical values is greater at the outset than the experimental error, but these differences may be accounted for by assuming that the ionisation ratio of the two radio-active types of matter varies, gradually assuming a smaller value, which is quite probable in view of the fact that the matter causing imparted activity is formed by the emanation, and the emanating power varies considerably with the nature and physical condition of the substance. Moreover, the presence of the emanation introduces experimental difficulties.

Considering now the ammonia separation, it was shown by Rutherford and Soddy that the filtrate residue simply contains ThX immediately after the separation, but ThX at once produces the inactive ThA, which, in turn, produces ThB, the last active product. This case differs from the one just considered, inasmuch as no ThA is present at the outset. Following the same notation as in the previous case, it is seen that n , the number of ThX atoms present at the time t , is obtained from $n = n_0 e^{-rt}$.

The rate of change in ThA is expressed by—

$$\frac{dn}{dt} = -r_1 n + rn,$$

which, upon integration, gives—

$$n_1 = \frac{r n_0}{r_1 - r} (e^{-rt} - e^{-r_1 t}).$$

The rate of change in ThB is expressed by—

$$\frac{dn_2}{dt} = -r_2 n_2 + r_1 n_1.$$

This equation, after substituting in it the value of n_1 when integrated, gives—

$$n_2 = \frac{r r_1 n_0}{r_1 - r} \left(\frac{e^{-rt}}{r_2 - r} - \frac{e^{-r_1 t}}{r_2 - r_1} \right) + \frac{r_1 r n_0}{(r_2 - r)(r_2 - r_1)} e^{-rt}.$$

The activity at the time t is given by—

$$I = rn + K r_2 n_2,$$

where K again represents the ratio of ionisation due to ThB.

The theoretical values in the table below were calculated from the last equation. In the calculation of the values of n_2 , the last term in the equation becomes negligible after the fourth hour. The value of $K = 0.44$, here employed, is the one given by Rutherford ("Radio-activity," p. 298).

Time.	Theoretical values.	Experimental values.
0	100	100
1 hour	100+	101
5 hours	105	106
10 "	111	110
16 "	116	117
20 "	115	117
24 "	114	113
50 "	103	100
3 days	89	88
4 "	75	73
8 "	37.7	38
12 "	18.8	19
20 "	4.7	5

Here again the maxima in the theoretical and experimental values practically coincide, and the theoretical and experimental values show a close agreement throughout.

Removal of ThX by means of other Reagents.

Various qualitative tests were made with other reagents which precipitate thorium quantitatively from aqueous solutions of its salts. In many cases the residue obtained by evaporating the filtrate and igniting it was highly radio-active, showing that a radio-active constituent had been removed. The following additional reagents remove some

form of radio-active matter from thorium compounds: aniline, benzoic acid, meta-nitrobenzoic acid, tannic acid, potassium xanthogenate, hydrogen peroxide, piperidine, phenylhydrazine. In fact, the major part of the reagents tried, which precipitate thorium completely, yielded radio-active residues. The precipitates were also radio-active, thus showing that a non-separable portion of the activity is either due to thorium itself or to a new type of matter closely resembling thorium in its behaviour towards reagents. The distribution of the radio-active components between the precipitate and residue, when the above reagents are used, is being studied, and in this connection the separations are being conducted with a sample of thorium nitrate which has been specially purified.

Although no very accurate tests on the emanating power of the different thorium precipitates were carried out, still the values observed show that the different compounds vary considerably in this respect. Rutherford and Soddy first directed attention to this point (*Journ. Chem. Soc.*, 1902, lxxxi., 851). They found that when thorium was precipitated apparently under the same conditions the precipitate often showed marked difference in emanating power. The thorium oxide obtained by us by means of pyridine generally possessed less emanating power than the oxide obtained by means of ammonia. The thorium fumarate precipitate possessed a high emanating power. Although it varied considerably it was usually more than twice that of the ammonia precipitate. Hence thorium fumarate exceeds in emanating power any of the other thorium compounds thus far examined.

Summary of Results.

1. The separation of the radio-active types of matter in thorium compounds by chemical methods was studied from a qualitative standpoint, and a detailed quantitative study was carried out with two reagents—pyridine and fumaric acid.

2. The removal of ThX from thorium compounds by means of ammonia, discovered by Rutherford and Soddy, was confirmed. Our experiments constitute an extension of the method of separation employed by these investigators.

3. Pyridine and fumaric acid remove from thorium nitrate solution ThX and the inactive product, ThA, of the matter which constitutes the imparted activity of thorium. The precipitate contains the non-separable activity and the radio-active component of the imparted activity, ThB, which decays to half value in fifty-five minutes.

4. It was shown both by experimental and theoretical considerations that the presence of ThA in the filtrate residue, in the separation by means of fumaric acid, and its presence in the precipitate when ammonia is employed, accounts for the initial differences observed in the curves of decay and recovery of the separated products.

5. ThA was isolated from the other radio-active products by chemical methods. Pure ThB was isolated by electrolysis.

6. Inactive thorium was not obtained in the course of the experiments.

7. One precipitation of an aqueous solution of thorium nitrate with fumaric acid yields a thorium precipitate whose activity at the end of five hours is less than one-fourth the final activity of the product.

8. The emanating power of thorium fumarate was found to be approximately double that of the thorium oxide obtained by precipitation with ammonia, while the emanating power of the oxide obtained in the pyridine precipitation fell below that obtained by the use of ammonia.

Further experiments on the separation of the radio-active products in thorium compounds by chemical methods are in progress.

Correction.—In the Obituary Notice in our last issue (p. 28), the date of the decease of the late Dr. Sprengel was incorrectly given as Friday, January 12th, instead of Sunday, January 14th.

MECHANICAL ANALYSIS OF SOILS.

A SUGGESTION FOR A LONG TUBE SEDIMENTATION PROCESS.

By J. ALAN MURRAY.

THE importance of finding some quick and handy method of "sorting out the particles of soil into groups each of which contains material lying between specified limits of size" is generally recognised. The method of Hall and Luxmore revised by Hendrick described in a recent paper, whatever its merits in other respects, cannot be described as either quick or handy. To effect a complete separation of the finer from the coarser particles by mixing the soil with water and decanting off the portion which remains in suspension after standing some time, requires repeated washing of the sediments. This occupies a long time, and involves the accumulation of much water which must be subsequently evaporated.

The repeated washing of the sediments is of course indispensable, because when the particles of soil are suspended in water and allowed to settle, some of the smaller particles near the bottom are deposited sooner than some of the larger ones which have a greater distance to travel. The depth of the column of water employed is purely arbitrary, but no variation in the depth of the column will obviate this difficulty; in fact, since the particles are more or less uniformly distributed through it, the longer the column the more incomplete will be the separation.

But if a fairly long column of water be taken—say, about a metre—and all the particles start from the top at the same time, then the largest will reach the bottom first and the others after longer intervals according to size.

To make a separation in this way it is necessary to devise some means by which a quantity of liquid containing the fine soil in suspension can be introduced at the top of such a long column of water, and by which the fractions may be removed as they collect at the bottom. In order to admit of the removal of the fractions the tube must be open at the bottom and consequently must be closed at the top. All attempts to introduce the liquid containing the soil in suspension by means of side tubes, stopcocks, &c., failed owing to the considerable downward pressure of the column of water. It is, however, quite simple to introduce the liquid at the bottom of the long tube, and then invert it. This comes to the same thing, and it was in this way that the more successful experiments were conducted.

The apparatus employed consisted of a pear-shaped flask (*i.e.*, one having a very sloping shoulder) of about 200 c.c. capacity; from this a portion of the neck was cut off, leaving a piece (about an inch and a-half) just long enough to insert through an indiarubber cork, by means of which it can be attached to a long piece of glass tubing. The tube actually used was one which happened to be in the laboratory, and which proved on measurement to be 1.47 c.m. long by 2.3 c.m. internal diameter. A wide shallow glass basin about 20 c.m. diameter and a few small porcelain evaporating dishes about 7.5 c.m. diameter are also necessary. It was found, however, that notwithstanding the shape of the flask there was some tendency for the finer particles to lodge on the shoulder, and it was later replaced by an Erlenmeyer's flask of which the neck, after removal of the flange, was exactly the same diameter as the tube. This was attached by means of a piece of indiarubber tubing fitted outside of the tube and of the neck of the flask.

The experiment was carried out as follows:—Five grms. of the air-dried fine soil (*i.e.*, that which had passed through 100 mesh sieve), thoroughly disintegrated in dilute ammonia solution, was put into the flask, which was then vigorously shaken, filled nearly full of water, and attached to the tube. Water was then poured gently down the side of the tube (so as not to disturb the sediment in the flask) till it also was full, when the open end was closed with a cork, and the whole inverted over the large basin of water.

EXAMPLE I.—Showing Results obtained in Three Trials with a Stiff Clay Soil, Untreated with Acid, after Rough Preliminary Separation into Coarse and Fine Material.

Fraction.	Time. Minutes.	Average diameter of particles. M.m.	Grms.			Per cent.		
			I.	II.	III.	I.	II.	III.
1.	5	0.13	0.420	0.535	0.374	8.40	10.70	7.48
2.	15	0.06	0.783	0.838	0.660	15.66	16.76	13.20
3.	40	0.03	0.923	0.980	0.952	18.46	19.60	19.04
4.	60	0.02	0.708	0.572	0.759	14.16	11.54	15.81
5.	180	0.013	0.590	0.542	0.569	11.80	10.84	11.38
6.	480	0.006	0.590	0.431	0.634	11.80	8.62	12.68
7. Residue		0.002	0.920	0.920	0.880	18.40	18.40	17.60
Moisture			0.205	0.205	0.205	4.10	4.10	4.10
			5.139	5.003	5.033	102.78	100.50	100.66

EXAMPLE II.—Showing Results obtained in Duplicate Trials with Rothamsted Soil (Plot 1 C, Barnfield, 1903), after Treatment with Acid, as recommended by Hall. No Preliminary Separation.

Fraction.	Time. Minutes.	Rate of falling. C.m. per Sec.	Average diameter of particles. M.m.	Grms.		Per cent.	
				I.	II.	I.	II.
1.	2.6	= 1 " 1	0.16	0.223	0.229	4.46	4.58
2.	13	= 1 " 5	0.05	1.545	1.523	30.90	30.46
3.	26	= 1 " 10	0.04	0.955	1.043	19.10	20.86
4.	52	= 1 " 20	0.025	0.707	0.644	14.14	12.88
5.	130	= 1 " 100	0.020	0.427	0.442	8.54	8.84
6.	260	= 1 " 400	0.010	0.203	0.111	4.06	2.28
7. Residue			0.004	0.531	0.662	10.62	13.24
Loss on solution				0.352	0.352	7.04	7.04
Moisture				0.150	0.150	3.00	3.00
				5.093	5.159	101.86	103.18

The cork closing the end was immediately withdrawn, and one of the small porcelain evaporating dishes, previously dried and weighed, placed beneath the open end of the tube.

The sediment began to descend whenever the tube was inverted, and the first particles were deposited in the dish in about fifteen seconds. After a short interval this dish, containing the first portion, was removed and replaced by another, and this again by a third, and so on. These dishes containing the several fractions of the sediment thus removed from the large basin were of course full of water, of which, however, a considerable part was separated by simple decantation, after standing for a few minutes, and the remainder driven off on the water-bath. The dried residue was then weighed, and examined under the microscope for determination of the size of the particles.

The small dishes (in which the fractions of sediment are collected) being entirely submerged in the water in the large basin, great care must be exercised in changing them, for, if the water be agitated, the fine sediment, which is easily disturbed, at once diffuses through the water, and is lost to the fraction to which it properly belongs. It was found, however, that with a little practice this operation could be easily and quickly performed without appreciable loss.

It was noticed in the course of the experiments that some of the particles falling through the column of water are caught and carried up again by ascending currents, of which the cause has not been ascertained or any means of preventing them. That they are due to some extent to the motion of the falling solid particles is probable, but it seems unlikely that this is the sole cause. Careful observation of individual particles showed that under favourable circumstances they never rose more than about $2\frac{1}{2}$ inches before they again took a downward course. Possibly a series of short downward pointing inner tubes or even ribs on the long tube would reduce the currents to a minimum.

Examination of the fractions under the microscope showed that while each consisted of particles of fairly uniform size, still some of the finest particles could be discerned among the coarsest. The finer particles may have

simply adhered to the larger ones, or they may have been drawn downwards in the wake (as sailors say) of the latter. Probably both causes combined to bring about the result. At all events the fact suggested the expediency of making a preliminary rough separation of the coarser and finer material, and this further modification was accordingly introduced in the later experiments as follows:—The fine soil after being disintegrated in weak ammonia solution was allowed to stand for fifteen minutes, and the water containing the finer material in suspension then poured off. The coarser material remaining in the beaker was then introduced into the flask, and the process carried out as previously described. Three fractions were collected. The first five minutes after the first particle had reached the bottom, the second fifteen minutes (*i.e.*, ten minutes after the first dish had been removed), and the third forty minutes from the commencement (*i.e.*, twenty minutes after the second dish had been removed). Almost the whole of the remainder of the coarser material was deposited within an hour; this, however, was not treated as a fourth fraction, but as fine material which had escaped through preliminary separation, and was accordingly returned to the beaker containing the finer material with which it was thoroughly mixed, and the whole introduced into the flask, and allowed to fall through the long column of water—the same water which had served for the separation of the coarser material being used over again so that there should be no loss of material which remained suspended in it. Three fractions were collected in this case also after one, three, and seven hours respectively, making six fractions in all. The liquid remaining in the flask and tube (containing what had not settled out in seven hours), amounting to a little over a litre, was measured, an aliquot part taken and evaporated to dryness, and a seventh and last fraction so obtained.

The value of the preliminary separation became at once apparent on examination of the fractions of the sediment, which were found to be much more homogeneous than before, though naturally a number of particles of exceptional size, above and below the mean, were always present in each. The mean or average size of the particles was,

however, readily recognisable—the same result being given repeatedly by independent observers. In fact, the mean size of the particles was so much more easily determined than the extreme limits that it has been found convenient to express the results in that form.

Should the process prove generally acceptable its utility would be greatly enhanced if a common basis for expression of results were agreed upon; that of a simple statement of percentages falling at a mean rate of so many centimetres per second has much to recommend it.

In the earlier experiments the sample of soil used was a stiff clay—it has actually been used for making bricks—which it was thought would present all difficulties likely to be met with. As it contained but little lime or organic matter, and the object at that stage was merely to test the method of separating the particles of different sizes, it was thought better to omit preliminary treatment with acid. The degree of accuracy with which the process can be carried out may be judged by comparison of the results obtained after experience had been acquired. Some of these results are given in the table, both in percentages and in actual weights of the fractions. More recently the process has been tried with a sample of Rothamsted soil (Barnfield plot, 1 C, first 9 inches, taken in 1903) after preliminary treatment with acid as recommended by Hall. The results are given in the form suggested above, *i.e.*, percentages of particles falling at a given rate per second.

This soil being so much lighter in character it was found unnecessary to make a preliminary separation into coarse and fine material.

It is difficult to compare the results with those obtained by Hall with the same soil, but it is evident that they differ considerably in regard to the proportions of the finest and coarsest material, and to a less degree in regard to the proportions of the intermediate groups. The correspondence between the duplicates is, however, fairly satisfactory.

THE TEMPERATURE OF SOLUTIONS HEATED BY OPEN STEAM.*

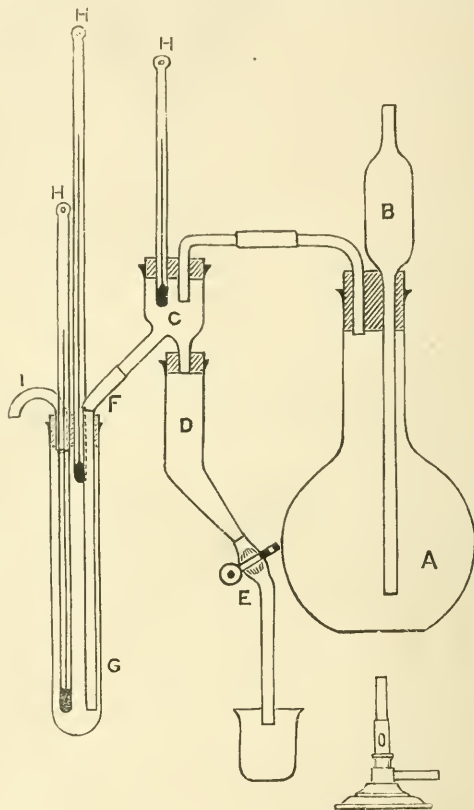
By THOS. STEEL, F.C.S., F.L.S.

THE fact that it is possible to heat solutions by means of open steam to temperatures higher than that of the steam itself does not appear to be so well known as its interest and importance warrant. I have not seen any direct reference to this point in works on physical subjects, and, indeed, am only aware of two references thereto in literature. The first allusion with which I am acquainted is in "Report of the British Association," 1869, *Trans.*, lxxv., and 1870, *Trans.*, lxiv., where Peter Spence records his accidental discovery of the phenomenon, and gives results of a series of laboratory experiments on the determination of the boiling-point of saturated solutions of various salts by blowing in steam at 100° C. Spence gives no explanation of the cause of the phenomenon, but contents himself with recording the results of his experiments. The other reference to the matter occurs in a recent publication, *Zeit. Ver. Deuts. Zucker-Ind.*, 1904, 1159, in a paper by H. Claassen on the "Boiling-point of Sugar Solutions." (See *Journ. Soc. Chem. Ind.*, 1904, 1105 and 1228). In this paper Claassen points the fact out clearly, and gives a brief theoretical explanation.

It is my purpose in the present paper to give a description of an apparatus which I have used, with details of some illustrative experiments, and to explain the theoretical considerations governing the phenomenon under discussion.

In the accompanying illustration of the apparatus used, A is a 32 oz. flask fitted with a 100 c.c. pipette; B is a safety tube; C is a tube for removing water from the steam

and allowing the temperature of the latter to be observed; D is a tube in which condensed water may gather; E is a rubber joint fitted with a spring clip, connecting to a tube leading to a small beaker placed beneath; F is a rubber joint connecting the tube which leads the steam into the large test-tube G; H, H, H, are thermometers; and I is a tube for carrying off surplus steam. When the apparatus is in use C is wrapped round with a piece of cotton-wool, while the tube G is inserted into a cylinder packed with the same insulating material. The water in the flask A is boiled, the clip at E being left open until the apparatus is warmed up and steam issues freely. As water accumulates in the tube D during the course of the experiments, it may be discharged by opening the clip. On placing a solution in the tube G and allowing the steam to pass through it, the temperature will rise steadily until a point is reached



at which it will remain for a time, and then gradually fall. If the steam be allowed to escape at any moment by opening the clip at E, and the tube G be removed with its fittings in place, and heated to boiling over a lamp, the temperature reached will, as a rule, be very little higher than that which was attained by means of the steam. In many cases, by having a quantity of the powdered salt present so as to keep the solution in a saturated state, the boiling-point of a saturated solution, or a temperature very near that point, may be readily reached and maintained. Under the conditions of my experiments the steam passing through the tube C has a temperature of 99.0°, which rises to 99.2° or 99.3° when subjected to the hydrostatic pressure in the tube G. The steam escaping from G has a temperature of 99.0°. Some scraps of platinum foil or bits of porous clay pipe are in all cases placed in the solutions for the purpose of promoting steady boiling.

In the following table the temperatures attained by some non-saturated solutions, when heated by steam under the

* From the *Journal of the Society of Chemical Industry*, xxiv., No. 11.

above conditions, are stated, as also the temperatures at which the same solutions boil when heated over a lamp:—

Non-saturated Solutions.

	Boiling temperatures.	
	With steam.	Over lamp.
Disodium phosphate	103°0	103°5
Sodium carbonate	104°2	104°5
Potassium nitrate	105°5	106°5
Ammonium chloride	111°5	112°5
Sodium acetate	112°5	114°0
Sodium nitrate	117°5	118°5
Potassium acetate	147°0	152°0
Calcium chloride	149°2	150°0
Ammonium nitrate	155°0	156°0
Ammonium nitrate (stronger) ..	163°0	164°0

It will be noticed that in all cases the temperature reached by heating over the flame is somewhat higher than that attained by means of steam. The temperatures attained by the various solutions depend, of course, on the concentrations. With a strong solution of ammonium nitrate steam at atmospheric pressure is competent to raise the temperature to 163°. In carrying out this experiment steam was passed direct into moist ammonium nitrate, and the temperature mentioned was quickly reached in spite of the fact that there is a considerable cooling effect when this salt is dissolved.

Saturated solutions, as I have before mentioned, may be tested in the same way by having a quantity of the powdered salt present in the hot solution. In the next table are given the temperatures attained by the use of steam with saturated solutions of a number of salts, and, for comparison, the boiling-point of the same solutions as obtained by heating over the lamp and also as published in "Watts' Dictionary of Chemistry" and elsewhere.

Saturated Solutions.

	Boiling temperatures.		
	With steam.	Over lamp.	Boiling-points (a).
Potassium chlorate ..	103°3	103°5	104°2
Zinc sulphate ..	103°5	103°8	104°4
Sodium carbonate ..	105°2	105°5	104°6
Potassium chloride ..	108°0	108°2	108°3
Sodium chloride ..	108°0	108°2	108°4
Potassium nitrate ..	114°0	115°0	115°9
Ammonium chloride ..	114°0	115°0	114°2

(a) The boiling-point of a saturated solution of zinc sulphate is by Griffiths, and is given in "Corney's Dictionary of Chemical Solubilities," p. 459; that of potassium chloride is the figure found by Legrand and quoted in Clarke's "Rules, Tables, and Data," p. 369; all the others are given on the authority of Legrand in "Watts' Dictionary of Chemistry," vol. iii., p. 89.

As is the case with non-saturated solutions the temperatures reached by the use of steam are somewhat lower than those obtained by boiling over the lamp, while the latter figures are sometimes higher and sometimes lower than the published boiling-points for saturated solutions of the salts experimented with. In this connection it should be explained that the salts used by me were the ordinary commercial ones sold by reputable dealers for laboratory use.

When dealing with very soluble substances such as calcium chloride, the solubility of the salt prevents saturation being reached. When steam is blown into granular calcium chloride, a solution is formed having a temperature of 149°2, while by heating over the flame this solution boils at 150°. If a saturated solution of the same salt is prepared by stirring powdered calcium chloride into the above solution kept boiling over a flame, the pasty mass formed boils at 175°. If now the tube containing the hot saturated solution be quickly placed in the lagged holder, and

steam passed in, the solution does not remain at the same temperature, but steadily cools. If the steam be now turned off, the contents of the tube allowed to cool somewhat, and steam again turned on, the temperature rises to a few degrees below the point at which it stood in the first instance. With ammonium chloride, treated in the same manner, the steam merely passes through and does not form a solution, consequently the contents of the tube do not rise above the temperature of the steam itself. On adding a little water, a saturated solution is formed which becomes heated to a temperature of 114°0, or only 0·2° less than the boiling-point for a saturated solution of this salt given in "Watts' Dictionary," while on heating over the lamp it boils at 115°0, which is 0·8 higher. A saturated solution of zinc chloride is stated in "Watts' Dictionary" to boil at 172°. With the apparatus described it is possible, by starting with the powdered salt into which steam is passed direct, to heat a saturated solution in which is suspended an excess of the salt, as high as 177°. Doubtless, in this case the heating effect is aided by the heat of solution of the zinc chloride.

The theoretical explanation of the results of the experiments above described is comparatively simple. When water is heated the pressure exerted by its vapour increases until, on the attainment of boiling-point, it equals that of the atmosphere. The boiling-point of any solution under ordinary atmospheric conditions, is that temperature at which its vapour pressure is equal to the pressure of the atmosphere. The effect of the solution in water of any substance such as a salt is to reduce the vapour pressure of the liquid and hence to raise the temperature to which it must be heated before it will boil. It thus comes about that saline solutions have boiling-points higher than that of water. Now, when steam at the boiling-point of water is passed into a saline solution, the vapour pressure of the steam being equal to that of the atmosphere, but greater than that of the solution, the steam condenses in the solution and continues to do so as long as the latter has a lower vapour pressure—or, in other words, so long as the solution is not at boiling-point. When this point is reached the steam merely blows through the liquid, a sufficient quantity condensing to replace the heat lost by radiation, &c. It is to the liberation of the latent heat of the steam on condensation that is due the heating effect which we have been considering. When we reflect how great is the amount of this latent heat (some 537 calories for each c.c. of water condensed from steam) we can readily understand why such striking thermal effects are produced.

The fact of condensation taking place causes dilution of the solution with consequent reduction of boiling-point, unless a supply of the solid salt is maintained so as to keep the solution constantly saturated.

Taking into consideration all the facts, in my opinion the temperature to which a solution is heated by steam is a truer measure of its boiling-point than that obtained by the application of direct heat. It is well known that the temperature of boiling water varies within quite considerable limits, according to the nature of the vessel in which it is contained, and the boiling-point of liquids other than solutions of solids, is always determined from the temperature of the vapour. It is equally well known that saline solutions are very readily superheated when boiled over a flame, and it is highly probable that the boiling-point determined in this way will tend to be too high.

When alcohol of sp. gr. 0·816 is placed in the tube and steam injected, condensation takes place until the liquid becomes heated to boiling, and when this point is reached the liquid has a temperature of 79°1°, that of the escaping vapour being 78°1°. This difference is due to the fact that the vapour is richer in alcohol than the liquid, and accordingly, having a higher vapour pressure, comes away at a lower temperature. The fact that the water vapour escaping from a boiling saline solution has the same temperature as that from boiling water is due to the same cause.

While experimenting on heating saline solutions with steam, it is interesting to observe the effect on the thermometer placed in the vapour space of the boiling-tube when, through splashing, its bulb becomes covered with the saline solution. When a saturated solution of a moderately soluble salt is under observation and a portion of the liquid carrying particles of the solid salt splashes on to the thermometer bulb, the temperature at once rises to and remains at the same point as the boiling liquid itself. The film of saturated solution on the bulb, being enveloped in steam at 99° , behaves precisely like the mass of solution and maintains the thermometer at the boiling-point of the solution. Sodium chloride shows this extremely well.

The condensation of water from the atmosphere on particles of substances like sugar or salt, when the air is laden with moisture, is due to the same cause, the difference in vapour pressure of the film of solution adhering to the salt, and that of the moisture in the atmosphere, transference of water vapour always taking place in the direction of least vapour pressure. This was originally termed "invaporation" by Graham, who experimented with saline solutions in air saturated with water vapour, and determined the rate of condensation in the solutions (*Edinburgh Journ. of Science*, 1828, xvi., 249; *Report British Association*, 1886, 207).

In the course of some of my earlier experiments I used a vessel of boiling water in which to place the tube containing the solution under observation, but I quickly found that, far from being as efficient as the cotton-wool lagging subsequently used, the boiling water actually cooled the tube.

A knowledge of this property of steam whereby solutions are heated to temperatures considerably above that of the steam itself, may be of practical importance in chemical industries where saline solutions require heating to temperatures greater than 100° . Again, in some cases—as, for instance, in the course of operations in the manipulation of sugar and other organic substances—considerable over-heating may readily occur through the mistaken idea that the temperature of the steam used determines the limit of heating possible.

DISCUSSION.

Mr. W. A. DIXON said he had found that a steam spray immediately destroyed the prickly pear; was this partly due to the temperature being raised?

Dr. R. GREIG SMITH thought this matter had been explained in a clear and forcible way, and inquired what the temperature effect of direct steam on agar would be. This substance was used for bacteriological purposes, and could only be obtained as a solution after long and tedious digestion. Would direct steam hasten the process?

Mr. T. STELL, in reply, said the efficiency of steam in killing prickly pear would be due to liberation of latent heat and thorough distribution; but unless some of the steam diffused into the sap, the temperature would not rise above that of the steam itself. As regards the effect of direct steam on agar-agar, he had no doubt that this substance would behave in the same manner as a salt.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 26, December 26, 1905.

Researches on the Insoluble Potassium Compounds contained in Wood Charcoal.—M. Berthelot.—The action of dilute hydrochloric acid either hot or cold upon wood charcoal is to decompose the potassium and lime

salts of a certain insoluble acid, which latter is comparable with the acid produced during the action of the same concentrated hydracid on sugar. An investigation on this subject proves that in wood charcoal there exist two orders of alkaline and acid compounds which are equally stable. One series are immediately destroyed by dilute hydrochloric acid, the other being unattacked by this agent. Their properties and different affinities are analogous to those of the various classes of artificial and natural silicates, which behave so very differently towards acids.

Samarium Sulphates.—Camille Matignon.—Samarium sulphate can under suitable conditions be transformed either into an acid or basic salt. The anhydrous sulphate when added to excess of sulphuric acid and evaporated at about 200° leaves a residue of fine needle-shaped crystals of the basic salt, $\text{Sm}(\text{SO}_4\text{H})$. If this salt is calcined it is transformed into the neutral salt. When this neutral salt is heated to about 1000° it is transformed into the basic salt, $\text{Sm}_2\text{O}_3\text{SO}_3$. This latter is an amorphous powder very slightly yellow, and insoluble in water or cold dilute sulphuric acid.

Nickel Oxide.—H. Baubigny.—The author's series of experiments are to prove that MM. Bellucci and Clavari's theory of the non-existence of the oxides of nickel, Ni_2O_3 and Ni_3O_4 , is wrong, and that these oxides can be prepared.

Action of Acetylene on Anhydrous Iodic Acid.—George F. Jaubert.—The author investigates the action of acetylene gas on anhydrous iodic acid by using a U-tube containing some grammes of the anhydrous iodic acid heated to 80° in a water-bath, and examining the acetylene after this gas has been drawn through the tube by means of an aspirator. He finds that the substances act energetically on one another, and the iodic acid is reduced according to the equation $\text{I}_2\text{O}_5 + \text{C}_2\text{H}_2 = \text{I}_2 + 2\text{CO}_2 + \text{H}_2\text{O}$.

Action of Glucose on Selenious Acid.—MM. Echsner de Coninck and Chauvenet.—During the process of reduction of selenious acid by means of glucose a variety of amorphous red selenium is produced which is insoluble in pure carbon disulphide. This appears to be in a physical condition corresponding to a colloidal state. It can be transformed partially into black selenium at about 100° .

Action of Ammonia Gas on Tri-bromide and Tri-iodide of Phosphorus.—C. Hugot.—Yellow phosphorus amide, which is produced when ammonia acts on the tri-bromide and tri-iodide of phosphorus at a very low temperature, is not soluble in ammoniacal ammonium bromide. It can be isolated, and gives, when slowly decomposed, phosphorus imide. On the contrary, it is very soluble in ammoniacal ammonium iodide. Its decomposition when contained in this liquid is effected slowly, and causes the precipitation of the less soluble imide.

A New Method of Preparation of Barium.—M. Guntz.—Some years ago the author showed that a metal containing 98.5 per cent of barium could be obtained by the calcination of barium amalgam in a vacuum. In his present research he varies the condition of this preparation without arriving at a very much more satisfactory state of purity. However, the dissociation of pure barium hydride in a vacuum at about 1200° allows of the preparation of the chemically pure metal.

Some New Derivatives of Pentabasic Phosphoric Acid, $\text{P}(\text{OH})_5$.—P. Lemoult.—The author finds that corresponding to the first series of etherobasic compounds of the form $\text{R}'-\text{O}-\text{P}(\text{NHR})_4$ is a second series of compounds $\text{R}''-\text{CO}_2-\text{P}(\text{NHR})_4$, which is much larger than the first one. The terms $\text{R} = \text{C}_6\text{H}_5$ have only been obtained in the second case.

Syntheses in the Series of Symmetric Heptane-triols 1.4.7.—J. L. Hamonet.—The author showed in a previous research that the bromo- or iodo-ether oxides $\text{RO}(\text{CH}_2)_n\text{X}$ give magnesium derivatives $\text{RO}(\text{CH}_2)_n\text{MgX}$, if n is greater than 2. He also showed the part which these substances play in various syntheses, particularly in

passing from a normal biprimary glycol to its superior homologue. He now describes a new application of these magnesium derivatives to a series of syntheses in the symmetric heptanetriols 1.4.7.

Derivatives from the Hydrogenation of Carvacrol.—Leon Brunel.—The author's experiments show that at a temperature of 115–120° catalytic hydrogenation is very active. Carvacrol is entirely transformed into hexahydroaromatic alcohol if the time of contact between the mixture of carvacrol, hydrogen, and nickel is sufficiently prolonged. On the other hand, the different results obtained at varying temperatures show that at 160° a similar secondary reaction giving rise to a second alcohol takes place. This action consists in the transitory formation of the acetone corresponding to a carvacromenthol called carvacromenthone, $C_{10}H_{18}O$. Above 150° traces of this acetone are formed by catalytic dehydrogenation of a part of the carvacromenthol which is produced.

MISCELLANEOUS.

Royal Institution.—On Thursday next, February 1, at 5 o'clock, Mr. Benjamin Kidd begins a course of two lectures at the Royal Institution on "The Significance of the Future in the Theory of Evolution"; and on Saturday, February 3, at three o'clock, Mr. J. W. Gordon delivers the first of two lectures on "Advances in Microscopy." The Friday Evening Discourse on February 2 will be delivered by Prof. S. P. Thompson on "The Electric Production of Nitrates from the Atmosphere," and on February 9 by Mr. H. F. Newall on "Eclipse Problems and Observations."

Institute of Chemistry—Pass List of the January Examinations.—Of fourteen Candidates who entered for the Intermediate Examination, ten passed:—A. P. Davson; F. W. Foreman; W. Garsed; T. R. Hodgson, B.A. (Cantab.); T. J. Kirkland; A. Lathwood, B.Sc. (Lond.); B. D. W. Luff; J. F. Reid; H. Stanley, B.Sc. (Lond.); and F. Tattersfield. In the Final Examination for the Associateship (A.I.C.), of five examined in the branch of Mineral Chemistry, two passed:—E. R. Bullock, Assoc.R.C.Sc. (Lond.); and T. F. Cowie. Of four in Metallurgical Chemistry, two passed:—H. J. B. Rawlins, B.Sc. (Lond.); and Thomas Stenhouse, B.Sc. (Lond.), Assoc.R.C.Sc. (Lond.), A.R.S.M. Of four in Organic Chemistry, three passed:—W. P. Hayworth; F. H. G. Horsman, B.Sc. (Lond.); D. Spence, Ph.D. (Jena). Of twelve who entered in the branch of the Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following nine passed:—J. T. Cart, B.Sc. (Lond.); C. G. Gates, B.Sc. (Lond.); A. G. Holborow; Miss E. S. Hooper, B.Sc. (Lond.); S. J. Lewis, B.Sc. (Lond.); A. J. C. Lickorish; S. G. Liversedge; Miss E. A. Macadam; F. E. Thompson, Assoc.R.C.Sc. (Lond.). The Examiners in Chemistry were Mr. W. W. Fisher, M.A. (Oxon.), F.I.C., and Dr. G. G. Henderson, M.A., F.I.C. The Examination in Therapeutics, Pharmacology, and Microscopy was conducted by Dr. F. Gowland Hopkins, M.A., F.R.S., F.I.C.

MEETINGS FOR THE WEEK.

MONDAY, 29th.—Society of Arts, 8. (Cantor Lectures). "Modern Warships," by Sir William White, F.R.S., &c.

TUESDAY, 30th.—Royal Institution, 5. "Impressions of Travel in China and the Far East," by Prof. Edward H. Parker, M.A.

— Society of Arts, 8. "The Chemistry of the Painter's Palette," by Prof. J. M. Thomson, F.R.S., &c.

WEDNESDAY, 31st.—Society of Arts, 8. "The Garden City and the Cheap Cottage," by Thomas Adams.

THURSDAY, Feb. 1st.—Royal Institution, 5. "The Significance of the Future in the Theory of Evolution," by Benjamin Kidd.

— Society of Arts, 8. (Howard Lectures). "High Speed Electrical Machinery, with special reference to Steam Turbine Machines," by Prof. Silvanus Thompson, F.R.S.

— Chemical, 8.30. "Hydroxylamine- α - β -disulphonates (Structural Isomerides of Hydroxylamidosulphates or Hydroxylamine- β -disulphonates)," by T. Haga. "Studies in the Camphane Series—Part XXI. Benzene-diazo- ψ -semicarbazinocamphor and its Derivatives," by M. O. Forster. "Relation between Absorption Spectra and Chemical Constitution—Part I. Chemical Reactivity of the Carbonyl Group; Part II. The Quinones and α -Diketones; Part III. The Nitranilines and the Nitrophenols," by E. C. C. Baly and A. W. Stewart. "Action of Light on Benzylidenephénylhydrazine," by F. D. Chattaway. "Union of Chlorine and Hydrogen," by D. L. Chapman and C. H. Burgess. "Molecular Weight of Adrenaline," G. Barger and A. J. Ewins. "Critical Temperature and Value of ML/θ of some Carbon Compounds," by J. Campbell Brown.

FRIDAY, 2nd.—Royal Institution, 9. "Electric Production of Nitrates from the Atmosphere," by Prof. S. P. Thompson, F.R.S., &c.

SATURDAY, 3rd.—Royal Institution, 3. "Advances in Microscopy," by John W. Gordon.

TO CORRESPONDENTS.

"Salts," Hull.—Dissolve aniline dyes in varnish and apply to the articles to be coloured.

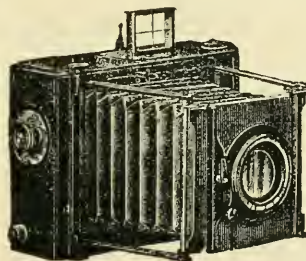
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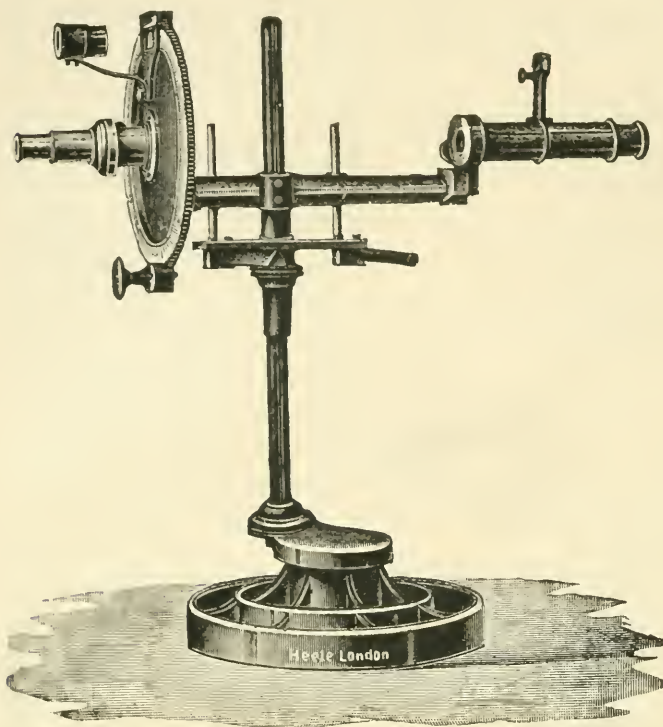
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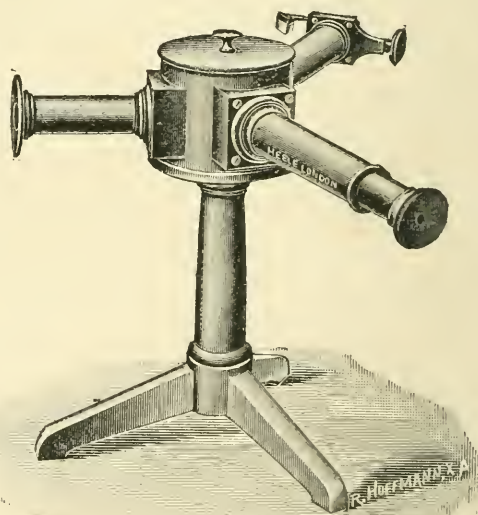
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THE CHEMICAL NEWS.

VOL. XCIII., No. 2410.

ON ANTI-FRICTION METALS HAVING LEAD AND TIN BASES.

By SERGIUS KERN, M.E., St. Petersburg.

THE practice of one of the principal engine-works in St. Petersburg showed that a babbitt, A, containing on the average 72 per cent of lead, 21 per cent of tin, and 7 per cent of antimony, used for three years in marine engines for lining heavy bearings, was especially good for the purposes intended.

The melting-point of this babbitt is $255^{\circ}\text{C}.$, the freezing-point $242^{\circ}\text{C}.$, leaving thus 13° for liquation effects. The last cypher represents an advantage of babbitt A over babbitts B and C, formerly used by the works, which have higher melting-points, but liqueur more freely.

Babbitt B contains on the average:—Lead, 70 per cent; tin, 15 per cent; antimony, 15 per cent; melting-point, $260^{\circ}\text{C}.$; freezing-point, $233^{\circ}\text{C}.$; for liquation effects, 27° .

Babbitt C contains on the average:—Lead, 77 per cent; antimony, 22 per cent; melting-point, $260^{\circ}\text{C}.$; freezing-point, $237^{\circ}\text{C}.$; for liquation effects, 23° .

All these babbitts have lead as a base, and so far as my experiments show me, such babbitts liqueur more freely in comparison with anti-friction metals having tin as a base.

In casting ingots of anti-friction metals we may clearly see, after analysing them, that such metals having a lead base give a more wide deviation in the percentage of elements entering into their composition, in comparison with metals having a tin base.

A certain moderate amount of lead is important in anti-friction metals with a tin base. It acts as "grease," and as a binding element between tin and antimony.

To show the preference of tin base babbitts, we give some particulars of an anti-friction metal for bearings, of which we prepared large quantities:—The metal contained on the average—Tin, 84 per cent; antimony, 2.15 per cent; lead, 6.25 per cent; and copper 7 per cent. This babbitt melts at $225^{\circ}\text{C}.$ and freezes at $221^{\circ}\text{C}.$, leaving thus very little for liquation effects (4°).

NOTE ON THE PRODUCTION OF OZONE BY ELECTROLYSIS OF ALKALI FLUORIDES.*

By E. B. R. PRIDEAUX, M.A., B.Sc.

WHEN a concentrated aqueous solution of hydrofluoric acid or of a fluoride is electrolysed, it is reasonable to suppose that the products of the action of nascent fluorine on the water will be ozone, hydrogen peroxide, or a hypofluorite.

With regard, first, to the formation of hydrogen peroxide, Skirrow found that none was formed on electrolysing a mixture of hydrofluoric and sulphuric acids (*Zeit. Anorg. Chem.* 1902, xxxiii., 25—30). Pauli states that no hydrogen peroxide can be detected after the electrolysis of an alkaline solution of potassium fluoride (*Zeit. Electrochem.* 1897, iii., 474—498). I have confirmed Pauli's result and also his statement that no hypofluorite is formed. As he does not mention how he tested for the hypofluorite, I may be pardoned for saying that the method employed by me was to add potassium iodide to both neutral and alkaline solutions after prolonged electrolysis

under varying conditions. Certainly some free iodine can always be estimated by means of N/100 sodium thio-sulphate, but in every case a blank experiment carried out under the same conditions gave practically similar numbers.

The production of ozone from aqueous solutions of KF and of HF might, conceivably, have some commercial importance. There are two memoirs bearing on this point. Pauli (*loc. cit.*) states that in the electrolysis of neutral and alkaline solutions of potassium fluoride ozone is formed in considerable quantities. His evidence for this, however, consisted only in the powerful smell and attack of his rubber connections. Now it is known that an extremely small percentage of ozone will give quite a strong smell, and those who have worked with ozone know to their cost that very little will instantly destroy rubber connections. It seemed desirable, therefore, to analyse the anode gas and see how much ozone could actually be obtained in this way.

Gräfenberg (*Zeit. Anorg. Chem.*, 1903, xxxvi., [3], 355—380) electrolysed aqueous hydrofluoric acid of the usual commercial strength, collecting the anode gas under a platinum hood and passing it up into a bulb full of potassium iodide solution. By varying the current density he obtained percentages of ozone varying from 0.475 to 3.48 by volume. Now 3.48 is a very high percentage of ozone. By the silent discharge method it is reckoned that a gas may be obtained containing 0.5 to 5 per cent of ozone, while the highest recorded percentages I have been able to find in the literature are 14.39 (Moissan, "Le Fluor et les Composés," p. 131, by the decomposition of water by pure fluorine), and 17.5 (McLeod, *C. R.*, xlix., 591, by the electrolysis of dilute sulphuric acid under carefully regulated conditions). Experiments were therefore tried to see if as much as 3 per cent of ozone could easily be obtained from aqueous hydrofluoric acid. I did not find that this was the case, the percentage of ozone using a current density of 100 ampères per (d.cm.)² being 0.23.

The electrolysis of potassium fluoride is more promising commercially than that of hydrofluoric acid, since potassium fluoride solutions are both easier to deal with and do not lose strength so rapidly by evaporation and attack of the containing vessel as solutions of hydrofluoric acid.

In the first experiments the potassium fluoride solution was contained in a U-tube of thin glass coated inside with a mixture of paraffin and vaseline. The kathode was of copper, the anode of platinum foil. The hydrogen and oxygen were at first collected to make sure of the yield of gas, afterwards the percentages of ozone were calculated from the number of coulombs which had passed. A tandem bubbler of potassium iodide solution was used to estimate the ozone. It was found afterwards that the ozone in no case got through the first bubbler; the second one was therefore dispensed with. The U-tube was immersed in ice-water. Varying the current density between 5 and 10 ampères per square d.cm. made scarcely any difference to the yield, which was, however, considerably affected by the duration of the experiment, falling off as this increased. The largest yield was 0.65 per cent of ozone in twenty minutes, the smallest 0.096 in four hours twenty minutes. The current density in both these experiments was 10 ampères per d.cm. Variation of current density from 5 to 10 ampères (ten experiments) made little difference; increasing it to 120 ampères, however, much increased the percentage of ozone, which now, with half an hour's run, was as low as 0.1 per cent. It thus appears that the yield of ozone from saturated potassium fluoride solutions at 0° is in all cases quite low, certainly not exceeding 1 per cent.

Lewis's Quarterly List (No. 24, October, November, December, 1905).—This number contains upwards of 150 titles of books, a considerable number of which would be of special interest to readers of the CHEMICAL NEWS.

* A Paper read before the Faraday Society, January 30, 1906.

THE NATURE OF ENZYME ACTION.*

By E. FRANKLAND ARMSTRONG, Ph.D., D.Sc., A.C.G.I.

ENZYMES are of the greatest importance biologically, as being the agents by means of which very many of the changes—both destructive and constructive—which take place in animals and in plants are brought about.

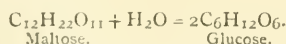
To the brewer, in particular, they have a wide significance, since they play a part in every stage of his daily work. It will, therefore, be at once granted, that for the proper scientific regulation of the technical process, it is essential to get as clear an idea of the nature of their action as possible.

When endeavouring to define an "Enzyme" the difficulty at once arises that no enzyme is as yet known in a pure state, or anything approaching it. In fact, all attempts to purify enzymes result sooner or later in the total loss of their activity; so that, even in the case of O'Sullivan's well-known investigations on the nature of invertase, there is no positive proof that the carbohydrate-like substances he isolated have anything to do with the specific activity of the enzyme. All that can at present be said is, that most enzymes can be obtained in an active state as white amorphous powders, soluble in water and containing carbon, hydrogen, oxygen, and nitrogen.

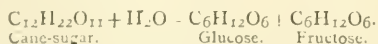
Generally speaking, they are active in presenting one or more molecules of water to complex substances and breaking them down into simpler compounds. They are non-living, inasmuch as they cannot increase by reproduction, differing in this respect from the yeasts, moulds, and bacteria. The so-called vital changes brought about by these latter agents are, however, now generally regarded as due to the enzymes they contain, and which they have in some way elaborated from their protoplasm.

Enzyme extracts or solutions of enzymes in water are conveniently prepared by grinding or shaking the particular animal or vegetable matter used with water or dilute alcohol in presence of an antiseptic to exclude bacterial contamination, toluene being by far the best. The active principle can be precipitated from such an extract by cautious addition of alcohol, though this procedure diminishes the activity. It is often necessary to rupture the cell wall by first drying the material and powdering it with glass or Kieselguhr before extraction, as the enzyme cannot diffuse through the undamaged cell wall.

Turning to the consideration of a few specific examples, it is found that the extract made by grinding up malt with water contains an enzyme—*diastase*—which converts starch into unfermentable dextrins and maltose, but is without further action on these products. Pressed yeast, dried by spreading it in thin layers on unglazed biscuit ware, when extracted with water yields an enzyme—*maltase*—which will convert a molecule of maltose into two molecules of glucose—



The dried yeast extract is also able to invert or hydrolyse cane-sugar, converting it into a molecule of glucose (dextrose) and a molecule of fructose (levulose)—



This change is brought about by an enzyme—*invertase*—the term inversion having been originally applied to the change to denote the change in the optical rotatory power of the solution as the cane-sugar, which has a positive rotatory power, is converted into the mixture of the two sugars having a negative rotatory power.

It would seem therefore that yeast extract contains two different enzymes: it may be well at this point to consider

briefly the evidence for believing that the two enzymes are really different.

(a) If a yeast extract be precipitated with alcohol, and the precipitate be re-dissolved in water and the process be repeated once or twice, an extract is obtained which, though it is still capable of hydrolysing cane-sugar, is quite without action on maltose. Similarly, an extract, prepared by allowing yeast to stand for a few days until it becomes liquid, then precipitating the enzyme carefully by means of alcohol and dissolving this precipitate in water, will attack cane-sugar only, and not maltose.

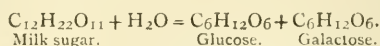
(b) A cold water yeast extract when used at high temperatures—above 40° C.—loses its power of hydrolysing maltose. Thus the power of the yeast extract to hydrolyse cane-sugar can be retained when its action on maltose has ceased.

(c) Further, such peculiar races of yeast as *Saccharomyces Marxianus* and *Saccharomyces Ludwigi* when dried furnish extracts which do not contain any maltase, though still able to invert cane-sugar and therefore containing invertase.

(d) Whereas, yeasts such as *Schizosaccharomyces octosporus* and *Saccharomycopsis capsularis* (extracts from which hydrolyse maltose with ease) are entirely without action on cane-sugar, i.e., they contain no invertase.

It is thus possible to obtain yeast extracts which sometimes contain invertase and no maltase, sometimes maltase alone, sometimes both enzymes. No clearer proof that the two enzymes in question are distinct substances can be desired.

As a further example the enzyme *lactase* may be cited. This converts milk sugar (lactose), an isomeride of cane-sugar and maltose, into two sugars, glucose and galactose:—



It occurs in the so-called Kefir grains and also in some rare varieties of yeasts such as *Saccharomyces fragilis*. Neither invertase nor maltase has any action on milk sugar, whilst the lactase extract does not hydrolyse maltose.

There is thus every proof that lactase, maltase, and invertase are distinct enzymes.

The biase sugars, maltose and cane-sugar, just dealt with, are known to the brewer as fermentable sugars. It is important to be quite clear, however, that in reality fermentation can only take place after the biase sugar, through the agency of the appropriate enzyme, has been converted into the simpler C₆ sugars. Hydrolysis must precede fermentation: the only directly fermentable sugars are glucose, fructose, galactose, and a somewhat rarer sugar—mannose—all of which have the same composition, C₆H₁₂O₆. In proof of this, the fact may be advanced that although *octosporus* yeast ferments glucose and fructose easily, it is quite without action on cane-sugar. When, however, a single drop of an invertase extract is added a brisk fermentation sets in, proving that inversion of the cane-sugar is necessary before fermentation can take place. In like manner, *Marxianus*, which ferments glucose strongly, cannot ferment maltose until used along with a maltase extract. The addition of an invertase extract containing no maltase has no effect. Similarly, it is impossible to ferment milk sugar by any yeast which does not contain lactase, unless a lactase extract be also used first to hydrolyse the biase.

The foregoing illustrations afford definite proof, not only that the various enzymes mentioned differ from one another, but that a different specific enzyme is required to hydrolyse each material. The action of enzymes may be said to be *selective*, and to differ therefore from the action of acids. Any one acid—such as hydrochloric acid—can hydrolyse any and all of the biase sugars or starch or similar compounds, though, it is true, with different degrees of readiness, whereas it has been shown that invertase acts on cane-sugar only.

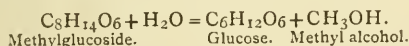
* From the *Journal of the Institute of Brewing*, xi., No. 6, July—
cpt., 1905.

Having established that maltose is affected only by maltase, it becomes of interest to ascertain whether any other substances can be found which maltase will act upon, and, if so, to determine the relationship that such compounds bear to maltose. It was not until certain developments which could be utilised had taken place in synthetical chemistry that this step forward could be realised.

By the interaction of glucose and methyl alcohol in presence of hydrogen chloride, a substance— $C_7H_{14}O_6$ —termed methylglucoside, is formed; whilst at the same time, as is so often the case in chemical reactions, an isomeride (that is a substance possessing the same constitution but differing in physical properties) is obtained.

These two isomeric methylglucosides are distinguished by the prefixes α - and β -.

Maltase readily converts the α -methylglucoside into glucose and methyl alcohol:—

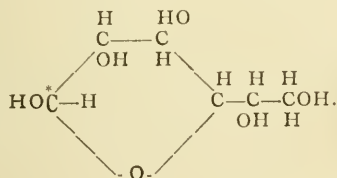


but is totally without action on the β -isomeride. The enzyme can therefore discriminate between the two isomerides. In order to realise the full significance of this fact a few words must be devoted to the structure of these compounds.

The β -methylglucoside, though not affected by maltase, can be hydrolysed by means of *emulsin*, an enzyme obtained by macerating sweet almonds with water. *Emulsin* also hydrolyses amygdalin and many of the natural glucosides, but it is totally without action on either α -methylglucoside or maltose.

Thus *emulsin* or maltase afford a ready means of distinguishing α - or β -methylglucosides.

The behaviour of glucose, $C_6H_{12}O_6$, the parent substance of the glucosides, is best denoted by the following structural formula,* which I have elsewhere given reasons for (*Trans. Chem. Soc.*, 1903, 1310; 1904, 1044).



The methylglucosides are derived from this by substituting an OCH_3 group for the OH group attached to the carbon atom marked*. This carbon atom is what is known as asymmetric, in that it has four different groups (*a b c d*) attached to it. These groups can obviously be written in order either clockwise—



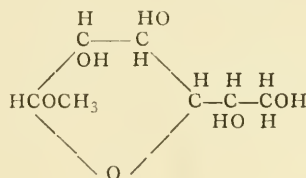
or counter-clockwise—



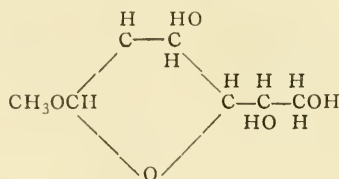
Two different forms are therefore possible, related as object to image, and they are termed stereoisomerides.

The isomeric methylglucosides are related in this manner; the difference between them may be represented by writing the OCH_3 group either to the right or to the left

of the carbon chain and the H on the other side. We do not at present know which of these represents the α - and which the β -form, but it is convenient here to label them—



α -Methylglucoside.



β -Methylglucoside.

The properties of the two glucosides are compared in the following table:—

	α -Methylglucoside.	β -Methylglucoside.
Melting-point	165°	104°
Optical rotatory power . . .	$+157^\circ$	-33°
Behaviour towards maltase .	Hydrolysed.	—
Behaviour towards <i>emulsin</i> .	—	Hydrolysed.

The action of the enzyme on these glucosides is to eliminate the OCH_3 and replace it by OH. It appears that the fact that this OCH_3 is sometimes on the one side of the molecule and sometimes on the other is enough to render the hydrolysis impossible. It may well be supposed that the maltase is attracted to the α -glucoside molecule, as pictured above, on its right-hand side, and can then hydrolyse the α -glucoside: that it is incapable, however, when so attached of acting on the OCH_3 group should this be in the β -position on the other side of the molecule. Similarly, perhaps, *emulsin* is attached to the left-hand side of the molecule and can then deal with the OCH_3 group in its left-hand or β -position, but it is quite out of harmony with this group in its right-hand or α -position.

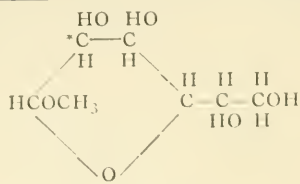
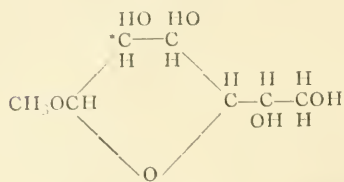
Such a simple conception as the above affords a complete explanation of the differential attack of the α - and β -glucosides; it involves, however, one assumption of fundamental importance, namely, that the enzyme becomes attached to the glucoside it hydrolyses.

A large number of experimental facts in favour of this view have been brought forward. It will here suffice to point out the very close connection between molecular structure or configuration, as it is termed, and liability to attack by enzymes.

Referring to the structural formula for glucose, it will be seen that each carbon atom has an OH and H radicle attached to it. Just as interchange of the position of the OCH_3 and H radicles on the asymmetric carbon was shown to produce two isomerides, so interchange of the OH and H on any other of the asymmetric carbon atoms in glucose will produce a new isomeride. In all sixteen isomerides of glucose related in this manner are possible, and no less than thirty-two isomeric glucosides. Relatively few of these compounds occur naturally; a number have been synthetically prepared by Emil Fischer, so that no less than eleven of the possible sixteen isomerides of glucose and many of the glucosides are known.

The two methylmannosides may be represented by the following formulæ:—

* Strictly speaking, glucose in solution is a mixture of two isomerides having the same relationship as the α - and β -glucosides.

 α -Methylmannoside. β -Methylmannoside.

It will be seen that they differ from the α - and β -methylglucosides only in respect to the relative positions of the groups attached to the carbon atom marked * contiguous to that to which the OCH_3 is attached. This slight difference, however, is enough to make both mannosides absolutely resistant to the attack of either maltase or emulsin, and as yet no enzyme is known which will hydrolyse them.

In general, any other change in the configuration of the molecule is found by experiment to render the resulting glucoside incapable of being attacked by any known enzyme, and the same applies to compounds derived from sugars, either with one carbon atom less in the chain, as arabinose or xylose ($\text{C}_5\text{H}_{10}\text{O}_5$) or with a carbon atom more, such as glucoheptose ($\text{C}_7\text{H}_{14}\text{O}_7$).

Lastly, the methylglucosides derived from *l*-glucose, the mirror-image of ordinary or *d*-glucose, both resist the action of either maltase or emulsin.

These illustrations will suffice to show the very intimate relationship which exists between an enzyme and the substance it acts upon: this can only be explained by supposing some form of combination between the two. The enzyme, moreover, must fit the glucoside at every point along the chain of carbon atoms. The combination may perhaps be compared to the way in which the successive fingers of a glove fit on to a right hand; if the position of any one finger be altered, it is impossible to fit the glove; further, the glove will not fit on the left hand.

Further evidence of the formation of some form of compound between enzyme and carbohydrate has been obtained by studying the action of maltase on maltose in the presence of a large number of other substances. It was found that of all the substances tried only glucose and the glucosides caused a retardation in the rate of change, presumably because these combined with the enzyme and so prevented part of it from acting on the maltose. All the other substances tested, although in many cases they differed only slightly from glucose, produced no appreciable effect, showing that any alteration in structure, however small, was sufficient to prevent combination with the enzyme.

It is perhaps necessary to point out that the actual hydrolysis of the carbohydrate is due to the action of the water molecules. The enzyme may be conceived, perhaps, as acting as a vice in presenting in the appropriate manner the water molecule to the centre to be hydrolysed.

The facts here discussed can be very easily followed by means of a solid model in which the affinities of the carbon atom are represented as emanating from the centre of a regular tetrahedron. When such a model is used, the alterations in the surface presented, produced by interchanging the positions of H and OH groups, are very striking.

A short discussion followed the reading of the paper.

A STUDY OF ROCK DECOMPOSITION UNDER THE ACTION OF WATER.*

By ALLERTON S. CUSHMAN.

In a previous publication the author has pointed out that when most rocks are crushed down to fine powders (100 mesh and finer) and then wetted, immediately hydrolytic reactions occur, which point indubitably to the fact that certain decompositions of the rock substance have taken place. Whenever, as is almost invariably the case in the rocks of igneous origin, alkaline bases, such as lime, magnesia, soda, and potash, are present, the fine powder will show an immediate alkaline reaction to delicate indicators, such as phenolphthalein, the instant the water comes in contact with them. Although these reactions start with remarkable promptness, they do not go far, and the actual amount of alkali set free is so small that few investigators have paid attention to the matter. Undoubtedly, however, as it is not difficult to show, these decompositions are of the very highest importance, not only in their relation to certain interesting theoretical considerations having to do with physical chemistry, but also because they have a direct bearing upon many important problems of engineering and of agricultural and industrial chemistry. The value of a rock for road building, so far as its binding or cementing power is concerned, depends entirely upon the fact that decomposition takes place. Since rocks, even of the same species and type, vary widely in their resistance to the action of water and dilute solutions when in the state of fine dust or powder, the value of such investigations as are detailed in this paper becomes apparent. Storer, from the standpoint of agricultural chemistry, discusses in a most interesting way the disintegrating power of water on rocks ("Agriculture in some of its Relations with Chemistry," 5th ed., vol. i., p. 134). Describing the work of the Messrs. Rogers, who found that from a third of 1 per cent to 1 per cent of some minerals was dissolved out by water, Storer calculates that, granting only one third of a pound of potash is dissolved out of every 100 pounds of rock, then in every 3,500,000 pounds which would go to make up an acre taken to the depth of 1 foot, about 10,000 pounds might be dissolved. Since 15 tons of good stable manure will supply no more to an acre than 150 pounds of potash alone, it is at once apparent that the immediate decomposition of certain potash-holding rocks under the action of water is a question of very high importance.

Daubree found that if felspar was ground in an iron cylinder for one hundred and ninety-two hours with water enough to make a thin slip, 0.4 per cent of potash could be found in solution at the end of the run. This result is in substantial agreement with numerous similar experiments which have been made in this laboratory. In the experiments about to be described, a typical orthoclase felspar from Westchester County, N.Y., was selected and ground dry in a ball mill until the powder all passed a 100-mesh screen. This powder had the following composition:—

	Per cent.
SiO_2	66.23
Al_2O_3	19.96
Fe_2O_3	0.25
K_2O	11.61
Na_2O	1.39
P_2O_5	0.39
$\text{H}_2\text{O } 100^\circ +$	0.28
	100.11

If this orthoclase dust was directly extracted with distilled water by shaking 25 grms. with 100 c.c. of distilled water and the mixtures subsequently filtered, about 0.024 per cent of soluble alkali was found by titration in the

* United States Department of Agriculture, Office of Public Roads, LOGAN WALLER PAGE, Director.

clear filtrate. The author has, however, shown elsewhere that by no means all of the alkaline bases set free by the decomposing action of water pass freely into solution. (See *U.S. Dept. Agr., Bureau of Chemistry*, Bull. No. 92). By subsequent action of some electrolyte, such as NH_4Cl , more of the base is carried into solution. This is shown in Table I. A number of samples were weighed out in Jena glass flasks, varying amounts of NH_4Cl added, and the contents thoroughly shaken with a measured quantity of water. Aliquot portions of the filtrates were evaporated to dryness, the residue heated to expel all ammonia salts, and weighed.

TABLE I.—Orthoclase Rock Powder treated with Dilute Solutions NH_4Cl .

Amount taken.	Strength NH_4Cl solution (100 c.c. used).	Weight of residue.	Residue per 100 grms.
Grms.	Per cent.	Grm.	Grm.
25	0.000	0.0060	0.0240
25	0.001	0.0092	0.0368
25	0.010	0.0184	0.0736
25	0.100	0.0400	0.1600
25	1.000	0.0624	0.2496
25	1.500	0.0664	0.2656
25	2.000	0.0608	0.2432

Table II. is included here to show that rock powders other than orthoclase are subject to similar decompositions. (See *U.S. Dept. Agr., Bureau of Chemistry*, Bull. No. 92).

TABLE II.—Diabase Rock Powder treated with Dilute Solutions NH_4Cl .

Amount taken.	Strength NH_4Cl solution (100 c.c. used).	Weight of residue.	Residue per 100 grms.
Grms.	Per cent.	Grm.	Grm.
25	0.000	0.0064	0.0256
25	0.001	0.0092	0.0368
25	0.010	0.0180	0.0730
25	0.100	0.0616	0.2464
25	1.000	0.1412	0.5648

The results included in these tables show the amount of soluble alkali that can be obtained in solution from the mere digestion of ordinary dry ground rock powders in cold water and dilute solutions of an electrolyte. If the powders are ground wet in a mill for a number of hours, more decomposition takes place, and more free alkali passes into solution. This is clearly shown in Table III.

TABLE III.—Orthoclase Rock Powder treated with NH_4Cl after Wet Grinding.

Amount taken.	Strength NH_4Cl solution (100 c.c. used).	Weight of residue.	Residue per 100 grms.
Grms.	Per cent.	Grm.	Grm.
25	0.000	0.080	0.320
25	1.000	0.118	0.472
25	1.000	0.125	0.500
25	1.000	0.132	0.528
25	1.000	0.143	0.572

The action of dilute solutions of ammonium chloride in causing an increased amount of free alkali to pass into solution has been discussed in a previous publication. (See *U.S. Dept. Agr., Bureau of Chemistry*, Bull. No. 92). The work of Linder and Picton (*Journ. Chem. Soc.*, 1892, lxi., 114, 148), Whitney and Ober (*Journ. Am. Chem. Soc.*, 1901, xxiii., 842), and others has shown that when colloid or pectoid substances are formed in the presence of solutions of electrolytes, the bases generally will be absorbed by the pectoid substance, if the pectoid is electro-negative in character. Although these absorbed bases can not be removed by water alone, they can be removed either wholly or in part by digestion in dilute solutions of certain electrolytes. The writer has shown that when water acts upon certain minerals and rocks, decomposition immediately commences, leading to simultaneous formation of pectoid matter and soluble electrolytes. We should therefore expect only a small portion of the alkaline bases

set free to pass freely into solution, which is precisely what we find to be the case.

If water attacks a mineral powder like orthoclase so readily, why, we may ask ourselves, does the reaction, practically speaking, come to a definite end almost immediately? The answer to this question is simple. Any reaction in which the reaction products are insoluble in water and are not removed by any agency from the surface of solid particles where they are formed, would behave in exactly this way. Remove the reaction products from the immediate place of formation, either by stirring, grinding, or by the action of certain electrolytes, and the reaction will proceed.

In spite of the general soundness of this reasoning, it was felt that experimental evidence was needed in order to get light upon the extent to which these decompositions actually take place. The vexatious difficulties experienced in trying to filter slimy suspensions, the effect of carbonic acid upon the indicator used in volumetric work, and, above all, the uncertainty as to the extent to which the soluble bases actually pass into solution, make investigations of this kind extremely difficult. It is probable, however, that the results obtained point the way to, even if they do not measure the quantitative limits of the reactions under discussion. It is certain that the kaolinisation of feldspars in nature proceeds to the conclusion of the decomposition reactions, but, although the process may be observed in some places as at present going on, we have no data on the time necessary to complete it, nor on the exact conditions in nature most likely to accelerate it. It may be surmised that the decomposition is extremely slow, and that natural attrition under the action of water is not so very much unlike the wet grinding operations of a laboratory mill.

In attempting to measure quantitatively the extent of the decomposition reactions as observed in the laboratory, there was always the danger that a portion, if not all, of the free alkali obtained already existed as such in the orthoclase sample, and was not therefore the result of the immediate decomposition induced by the action of the water. After some experimentation, a method was hit upon which seems in every respect suitable for testing the points just raised, as well as supplying an excellent laboratory method for the separation and analysis of various sorts of slimes and pectoid substances, which for obvious reasons are difficult, if not impossible, to filter. In our experiments, definite weights of the rock powders are slimed with a measured quantity of water, and the slime placed inside an ordinary unglazed porcelain cup such as is used for certain common types of bell batteries. An ordinary arc-light carbon is now inserted and the porcelain cup set down inside a glass cylindrical vessel containing distilled water to the depth of 2 or 3 centimetres. Another carbon electrode is then inserted in the outside compartment. The cell is now connected with a direct current of about 110 volts, the inner or slime chamber being in connection with the positive pole.

Under the action of electrical endosmosis all the liquid from the anode or slime chamber passes into the cathode chamber, while at the same time, owing to electrolysis, the free alkali passes out in a condition in which it can be easily titrated or otherwise estimated. In the course of a few hours the slime has been transformed into a hard, comparatively dry cake, while the free alkali has been partially removed. The alkaline liquor in the cathode chamber is now poured out into a beaker and titrated with tenth normal acid. After re-sliming the material in the anode chamber with the proper quantity of water, the apparatus is started again. With the conditions under which we were working it was found that about one hour sufficed for each run, and a series of runs was made, the results of which are shown in Table IV.

The results are seen to better advantage when plotted; the amount of alkali extracted by each run falls off rapidly until it practically reaches zero. The amount of current passing was approximately about 0.05 of an ampere when

the voltage was about 120. Another sample of orthoclase from an entirely different locality gave a very similar result.

Since it is quite possible by this method to extract practically all the free alkali which is contained in the slime, it is apparent that a re-grinding of the orthoclase and re-electrolysis will prove whether or not the alkali existed originally free in the orthoclase sample. In order to put this point to the test, the orthoclase charge which had been electrolysed to the end of the yield of free alkali was re-ground for several hours in a porcelain pebble mill. It was then slimed again with water, and re-electrolysed. *The results are conclusive as to the fact that the alkali which is obtained is set free by the immediate action of water, and is not originally a free constituent of the rock powder.*

The writer has contended in a number of publications that when most rock powders are acted on by water, only a portion of the soluble alkaline bases set free pass into solution, owing to the absorption by the pectoids which are also products of the decomposition. A mass of evidence of various sorts has been collected to support this view. This has a wide practical bearing, as it explains why the larger proportions of the bases are conserved during the natural process of rock disintegration, instead of being leached out and washed away. The results given above furnish additional proof of the truth of this contention. The fact that the actual amount of alkali extracted by the second electrolysis is larger than that extracted by the first is probably due to the increased surface effect resulting from the finer grinding. The equilibrium between the absorbent effect of the pectoids and the solvent effect of water requires further investigation. Orthoclase powder simply leached with water as is shown in Table I. yielded only 0.024 per cent of soluble alkali, whereas by endosmosis

TABLE IV.—Electrolysis of Orthoclase.
No. 1242.

Length of runs. Mins.	N/10 HNO ₃ taken. C.c.	KOH equivalent. Grm.	KOH extracted per 100 grms. Grm.
<i>First Electrolysis.</i>			
60	11.10	0.06216	0.03108
60	10.20	0.05712	0.02856
60	7.80	0.04364	0.02182
60	6.60	0.03696	0.01848
60	3.90	0.02184	0.01092
60	3.30	0.01848	0.00924
60	3.70	0.02072	0.01036
60	2.70	0.01512	0.00756
60	2.40	0.01344	0.00672
60	2.00	0.01120	0.00560
60	1.40	0.00784	0.00392
60	1.00	0.00560	0.00280
60	1.20	0.00672	0.00336
60	0.75	0.00420	0.00210
60	0.60	0.00336	0.00168
60	0.50	0.00280	0.00140
60	0.35	0.00196	0.00098
60	0.35	0.00196	0.00098
60	0.50	0.00280	0.00140
60	0.40	0.00224	0.00112
60	0.05	0.00028	0.00014
60	0.25	0.00140	0.00070
(a)	0.30	0.00168	0.00084
75	0.80	0.00448	0.00224
60	0.20	0.00112	0.00056
60	0.15	0.00084	0.00042
75	0.20	0.00112	0.00056
70	0.10	0.00056	0.00028
63	0.05	0.00028	0.00014
60	0.05	0.00028	0.00014
Total ..	62.90	0.35220	0.17610

TABLE IV.—Electrolysis of Orthoclase (continued).

Length of runs. Mins.	N/10 HNO ₃ taken. C.c.	KOH equivalent. Grm.	KOH extracted per 100 grms. Grm.
<i>Second Electrolysis.</i>			
60	13.30	0.07448	0.04598
60	15.00	0.08400	0.05185
60	13.00	0.07280	0.04494
60	8.50	0.04760	0.02938
57	5.80	0.03248	0.02005
60	4.10	0.02296	0.01417
75	4.40	0.02464	0.01521
60	0.80	0.00448	0.00277
60	0.30	0.00168	0.00104
60	0.20	0.00112	0.00069
60	0.20	0.00112	0.00069
(b)	1.50	0.00840	0.00519
Total ..	67.10	0.37576	0.23196
<i>Third Electrolysis.</i>			
60	6.50	0.03640	0.02459
60	17.00	0.09520	0.06432
60	17.50	0.09800	0.06622
60	15.50	0.08680	0.05865
58	11.60	0.06496	0.04389
58	11.20	0.06272	0.04238
58	10.70	0.05992	0.04049
60	7.80	0.04368	0.02951
60	5.50	0.03080	0.02081
60	3.50	0.01960	0.01324
60	2.30	0.01288	0.00870
60	2.30	0.01288	0.00870
60	2.10	0.01176	0.00795
60	1.75	0.00980	0.00662
60	1.80	0.01008	0.00681
63	1.40	0.00784	0.00530
60	1.40	0.00784	0.00530
60	1.65	0.00924	0.00624
62	1.00	0.00560	0.00378
60	0.90	0.00504	0.00341
60	0.70	0.00392	0.00265
60	0.70	0.00392	0.00265
60	0.80	0.00448	0.00303
60	0.60	0.00336	0.00227
(b)	0.70	0.00392	0.00265
60	0.70	0.00392	0.00265
60	0.25	0.00140	0.00095
62	0.25	0.00140	0.00095
60	0.10	0.00056	0.00038
(b)	2.10	0.01176	0.00795
Total ..	130.30	0.72968	0.49304
<i>No. 1300.</i>			
<i>First Electrolysis.</i>			
60	14.00	0.07840	0.03920
60	10.50	0.05880	0.02940
60	6.10	0.03416	0.01708
60	5.10	0.02856	0.01428
60	4.40	0.02464	0.01232
60	4.40	0.02464	0.01232
60	2.80	0.01568	0.00784
60	2.70	0.01512	0.00756
60	1.80	0.01008	0.00504
60	1.50	0.00840	0.00420
58	1.10	0.00616	0.00308
60	1.60	0.00896	0.00449
60	0.70	0.00392	0.00196
60	0.60	0.00336	0.00168
57	0.50	0.00280	0.00140
60	0.35	0.00196	0.00098
60	0.20	0.00112	0.00056
Total ..	58.35	0.32679	0.16339

TABLE IV.—*Electrolysis of Orthoclase (continued).*

Length of runs. Mins	N/10 HNO ₃ taken. C.c.	KOH equivalent. Grm.	KOH extracted per 100 grms. Grm.
<i>Second Electrolysis.</i>			
60	11.40	0.06384	0.03395
60	13.50	0.07560	0.04021
60	18.30	0.10248	0.05451
60	9.90	0.05544	0.02949
60	4.50	0.02520	0.01340
60	2.40	0.01344	0.00715
60	2.30	0.01288	0.00685
60	1.20	0.00672	0.00357
60	0.70	0.00392	0.00209
60	0.65	0.00364	0.00194
64	0.45	0.00252	0.00134
68	0.30	0.00168	0.00089
60	0.25	0.00140	0.00074
60	0.65	0.00364	0.00194
62	0.35	0.00196	0.00104
64	—	—	—
(a)	5.10	0.02856	0.01519
Total ..	71.95	0.40292	0.21430

Third Electrolysis.

60	35.00	0.19600	0.11137
60	11.90	0.06664	0.03786
60	2.80	0.01568	0.00891
62	1.80	0.01008	0.00573
60	0.70	0.00392	0.00223
60	0.40	0.00224	0.00127
60	0.30	0.00168	0.00095
63	—	—	—
243	0.90	0.00504	0.00286
(b)	4.40	0.02464	0.01398
Total ..	58.20	0.32592	0.18516

(a) Over Sunday.

(b) Over night.

it was possible to obtain 0.16 per cent. It is impossible to avoid the conclusion that the difference of about 0.15 per cent represents alkali absorbed by the pectoid aluminum silicate which the microscope reveals existing as cloggy films upon and among the rock particles when the action has been accentuated by wet grinding. Furthermore, the quantity of free alkali extracted by the action of electrolysis and endosmosis agrees sufficiently well with the quantity that is extracted from wet orthoclase by treatment with ammonium chloride.

Bredig and Schwerin have lately called attention to the value of the application of the principles of electrical endosmosis to certain practical problems (*Zeit. Angew. Chem.*, 1903, xvi., 581). The phenomenon was first studied by Wiedemann in 1852 (*Pogg. Ann. Phys.*, 1852, lxxxvii., 350), and it was shown that the power with which a galvanic current will drive a given liquid through a porous diaphragm of given area Q in the direction of the negative pole depends directly upon the hydrostatic pressure developed in the difference of level h , the intensity of the current J , the specific resistance of the liquid m , the thickness of the porous wall d , and inversely upon the area of the diaphragm. From these facts the following formula was derived:—

$$P = h = k \frac{J.m.d}{Q}.$$

The particular interest of this formula for the work in hand is that it seems to offer a possible method for studying quantitatively the relative amount of decomposition which takes place in various rock powders under the action of water.

Aside from its quantitative possibilities, electrical

endosmosis offers so efficient a method for separating not only water, but also acids or alkalis from slimy, colloidal, and otherwise unfilterable mixtures, that it is very surprising that it has not found a standard place both in the laboratory and in technical practice.

The question whether by this method, *i.e.*, successive grindings of orthoclase with removal of the alkaline decomposition products by electrical endosmosis, the kaolinisation of orthoclase and other rock powders can be carried on in the laboratory to the completion of the reaction as it undoubtedly is in nature, remains a field for future study. There would seem to be little doubt that it can be done. In any case, the present line of inquiry seems to offer an interesting and novel method for studying rock decomposition.

These investigations, of which this paper contains but a preliminary account, are being carried on, and will be presented in detail at some future time.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 18th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MESSRS. J. E. Coates, A. Amos, and M. B. Jack were formally admitted Fellows of the Society.

The PRESIDENT announced that the Society had lost a distinguished Fellow in the person of Professor Hermann Johann Philipp Sprengel, Ph.D., F.R.S., who was elected in December, 1864, and died on January 14th, 1906.

It was also stated by the President that the Society was indebted to Sir Henry E. Roscoe, F.R.S., for an important donation to the Library of nearly one hundred alchemical and old chemical works of great interest and value.

Certificates were read for the first time in favour of Messrs. Richard Victor Briggs, Sirseah Research Station, Mozuffierpore P.O., Bengal, India; Llewellyn Thomas Jones, B.Sc., Brenig View, Tregaron; Samuel Parfitt, 33, Partridge Road, Cardiff; Robert Le Rossignol, B.Sc., 2, Casarea Place, Jersey; Arthur William Thorp, 210, Sherborne Road, Yeovil; Henry Edgar Watt, B.Sc., 19, Summerhill Road, Dartford, Kent; Richard Willstatter, Ph.D., Bergstrasse 25, Zürich V.

Certificates have been authorised by the Council for presentation for ballot under By-law I. (3) in favour of William Mace, of Hope, Kingston, Jamaica; George Stanley Talbot, Ocean Island, Sydney, N.S.W.; Harry Sands Grindley, D.Sc., State University, Illinois, U.S.A.

The Council has ordered the following letter and report to be printed in the *Journal and Proceedings* of the Society:—

Government Laboratory.
Clement's Inn Passage, Strand, London, W.C.,
November 10th, 1905.

GENTLEMEN,—I have the honour to transmit to you the Report of the International Committee on Atomic Weights, 1906, to which I have appended the signatures of Professors Moissan and Seubert as desired by them.

It will be seen that the Committee, for the reasons stated in the report, are not prepared to advise any immediate alteration in the values for the atomic weights given in their last report. They recommend, however, in conformity with the desires of the great majority of the Larger Committee, that the values in the table for 1906 be given on the basis of $O = 16$, to the exclusion of those on the basis of $H = 1$.—I am, Gentlemen, your obedient Servant,

T. E. THORPE.

The Hon. Secretaries, the Chemical Society,
Burlington House, London, W.

Report of the International Committee on Atomic Weights.

During the year 1905 there has been unusual activity in the determination of atomic weights, and some of the work done relates to the most fundamental values. The entire system of atomic weights is thus affected more or less profoundly, and a general revision of the table would seem to be needed within the near future. Neglecting minor investigations, the more important determinations published since our last report are briefly as follows:—

Cadmium.—Atomic weight determined by Baxter and Hines (*Journ. Am. Chem. Soc.*, 1905, xxvii., 222), by analysis of the chloride. Three measurements of the ratio $\text{CdCl}_2 : 2\text{AgCl}$ gave in mean $\text{Cd} = 112.476$. Six measurements of the ratio $\text{CdCl}_2 : 2\text{Ag}$ gave in mean $\text{Cd} = 112.462$. General mean of both series, 112.469; when $\text{Ag} = 107.93$ and $\text{Cl} = 35.473$. As additional determinations are promised, based upon a study of cadmium bromide, a change in the atomic weight of cadmium as given in our table may properly be deferred.

Carbon.—From the ratios published in 1904, relative to the basic acetate and acetylacetonate of glucinum, Parsons (*Journ. Am. Chem. Soc.*, 1905; xxvii., 1204; *Zeit. Anorg. Chem.*, 1905, xlv., 215) has computed the atomic weight of carbon. The values obtained by treating the two ratios algebraically are $\text{C} = 12.007$ and $\text{C} = 12.007$. As the latter figure is quite independent of all previous determinations it has distinct corroborative significance.

Chlorine and Sodium.—In a very elaborate investigation upon the atomic weights of chlorine and sodium, Richards and Wells (published by the Carnegie Institution of Washington, 70 pp., April, 1905; see also *Journ. Am. Chem. Soc.*, 1905, xxvii., 459) have shown that the data furnished by Stas are affected by appreciable errors. Ten syntheses of silver chloride gave, in mean, $\text{Cl} = 35.473$ when $\text{Ag} = 107.93$. From ten measurements of the ratio $\text{Ag} : \text{NaCl}$, and ten of the ratio $\text{AgCl} : \text{NaCl}$, with the foregoing values for silver and chlorine, $\text{Na} = 23.008$. Stas's values are $\text{Cl} = 35.455$ and $\text{Na} = 23.048$.

The results just cited are obviously indirect, for they depend upon the atomic weight of silver. The experiments published by Dixon and Edgar (*CHEMICAL NEWS*, 1905, xci., 263) are therefore of peculiar interest, for they involve the intervention of no intermediate quantities between the atomic weights of chlorine and hydrogen. Hydrochloric acid was directly synthesised from weighed amounts of hydrogen and chlorine, and nine concordant determinations gave, in mean, $\text{Cl} = 35.195$, ± 0.0019 , referred to the hydrogen standard. With $\text{O} = 16$, Cl becomes 35.463, a value nearly midway between that found by Stas and the new figure given by Richards and Wells. Considering the difficulties of the work, the agreement between this and the previous investigations is as close as could be reasonably expected.

Gadolinium.—Urbain (*Comptes Rendus*, 1905, cxl., 583), from ten analyses of the octohydrated sulphate, finds $\text{Gd} = 157.23$; when $\text{H} = 1.007$ and $\text{S} = 32.06$. This value is more than a unit higher than that given in the table, and is probably more trustworthy. (See Eberhard, *Zeit. Anorg. Chem.*, 1905, xlv., 374, on the spectroscopic purity of the rare earth oxides studied by Urbain and others.)

Iodine.—Baxter has continued his research of 1904 upon the atomic weight of iodine, and has published a second memoir upon this subject (*Journ. Am. Chem. Soc.*, 1905, xxvii., 876). First, from eight conversions of silver iodide into bromide by heating in bromine, he found $\text{I} = 126.985$. Two series of measurements, of five experiments in each, of the ratio AgI to AgCl , gave respectively 126.982 and 126.284. Eight determinations of the direct ratio between silver and iodine, weighed separately, gave in mean 126.987. Five determinations of the ratio $\text{I} : \text{AgI}$ gave 126.983, and four of the ratio $\text{Ag} : \text{AgI}$ gave 126.989. The average of all six series is $\text{I} = 126.985$; when $\text{Ag} = 107.93$, $\text{Cl} = 35.473$, and $\text{Br} = 79.953$. The last of these antecedent values was checked by a direct comparison of AgBr with AgCl , and the mean of six experiments gave $\text{Br} = 79.953$. The value previously found by Baxter was 126.975 for

iodine, and the difference is partly due to his use, in the later investigation, of the new figure obtained for chlorine by Richards and Wells. The iodine work, therefore, is confirmatory of the latter.

Nitrogen.—R. W. Gray, in a preliminary notice (*Proc.*, 1905, xxi., 156), gives the results of his experiments upon nitric oxide. Ten determinations of the density of the gas, corrected by D. Berthelot's formula, give a molecular weight of 30.005, whence $\text{N} = 14.005$. Six analyses of nitric oxide, effected by burning finely-divided nickel in it, gave $\text{N} = 14.006$. The investigation was to be continued farther.

Guye, in an interesting lecture before the Chemical Society of Paris (*Bull. Soc. Chem.*, Aug. 5, 1905, with independent pagination; compare Richards, *Proc. Am. Phil. Soc.*, 1904, xliii., 116), has given a complete summary of the researches relative to this atomic weight, which have been conducted by him and his associates at Geneva. He also discusses, somewhat fully, all previous determinations of the constant, and concludes mainly from the physical evidence, that the atomic weight of nitrogen is not far from 14.01, and that the value 14.04, obtained by Stas, is no longer tenable. Going still farther, he reverses the ordinary gravimetric ratios from which the accepted atomic weight of nitrogen was derived, and, applying to them the new value for N , he deduces the atomic weight of silver. The latter is thus reduced from 107.93 to below 107.89, ranging even as low as 107.871. For these low values Guye cites much confirmatory evidence, which is not to be lightly disregarded. To this point we shall recur later.

Potassium.—Atomic weight re-determined by Archibald (*Trans. Roy. Soc. Canada*, Series 2, x., Section iii., p. 47) through analysis of the chloride. Four measurements of the ratio $\text{AgCl} : \text{KCl}$ gave $\text{K} = 39.139$, and four of the ratio $\text{Ag} : \text{KCl}$ gave 39.140; when $\text{Ag} = 107.93$ and $\text{Cl} = 35.455$. If $\text{Cl} = 35.473$, then K becomes 39.122.

Silicon.—W. Becker and J. Meyer (*Zeit. Anorg. Chem.*, 1905, xliii., 251; xlv., 45) have determined the atomic weight of silicon by conversion of the chloride into the oxide. Eight determinations were made, and, in sum, 46.82400 grms. of SiCl_4 gave 16.58236 grms. of SiO_2 . Hence, with $\text{Cl} = 35.45$, $\text{Si} = 28.207$. With the Richards-Wells value for chlorine, 35.473, Si becomes 28.257. Additional determinations by a different method are promised. This paper is preceded by an essay by Meyer on the calculation of atomic weights (*Ibid.*, p. 242), which deserves careful consideration.

Strontium.—From four measurements of the ratio $2\text{Ag} : \text{SrCl}_2$, Richards (*Proc. Am. Acad.*, 1905, xl., 603) finds $\text{Sr} = 87.661$, when $\text{Ag} = 107.93$ and $\text{Cl} = 35.473$. This confirms the earlier value derived by Richards from experiments upon strontium bromide.

Tellurium.—Gallo (*Atti Accad. Lincei*, 1905, [v.], xiv., 23 and 104) have determined electrolytically the ratio between silver and tellurium. From twelve experiments, in mean, $\text{Te} = 127.61$, when $\text{Ag} = 107.93$. Incidentally to this work, as a check upon the method employed, four comparisons between silver and copper were made. In mean, $\text{Cu} = 63.58$.

Thorium.—R. J. Meyer and Gumpertz (*Ber.*, 1905, xxxviii., 817) have attempted to separate ordinary thorium into fractions of different atomic weight, and have failed to verify the observations of Baskerville. The fractions obtained by various processes gave atomic weights varying from 232.2 to 232.7, values which are essentially identical with that given in the table.

From the foregoing summary of results, it becomes evident that a far-reaching series of changes will soon be needed in our system of atomic weights. A change in chlorine or nitrogen implies many other changes in the table, and if the accepted value for silver should be modified the alterations would be most sweeping. The atomic weights of silver, chlorine, and bromine enter into the calculation of nearly all other atomic weights, and form, so to speak, the platform upon which the entire structure stands.

The changes, however, which are suggested at present, are not final. Work is in progress in several laboratories which may confirm or modify many of the accepted values, and until that work is finished, at least so far as the fundamental data are concerned, it is wisest for us to suspend judgment and await developments. Were we to reconstruct the table of atomic weights on the basis of the evidence now before us, we should do it imperfectly, and a new revision would be demanded next year or the year after. Confusion would inevitably follow. Fortunately, the matter is not urgent, for the corrections which now seem desirable are not large, and the existing figures are accurate enough for all ordinary purposes. We therefore recommend that the table for 1905 be continued in use without change during 1906, even although some modifications are theoretically desirable. A year hence we shall be in a better position for a critical adjustment of the data, and no harm can follow from the delay. In accordance with the expressed wish of a majority of the larger committee, we also recommend that the table based upon the oxygen standard be made official. So far as this Committee is concerned, the private opinions of its members will be subordinated to the desires of the majority, and the table referred to hydrogen will no longer appear as a part of its report.

For the present, a few suggestions may not be unacceptable, which follow from an examination of the lecture by Guye. Rayleigh, Leduc, Guye, Gray, and others, from their studies of nitrogen and its oxides, have accumulated a mass of strong evidence in favour of a lower value for nitrogen. The data furnished by Stas, on the other hand, point to the higher value which has heretofore been generally adopted. Can we abandon one in the favour of the other, and accept the new figure without reserve?

On behalf of the new figure for nitrogen, we must admit that the determinations are remarkably concordant, and that they rest upon a direct comparison of the element with oxygen. The Stas values, with their confirmations by other chemists, are also very concordant, but they are indirect. They all rest primarily upon the atomic weights of silver, chlorine, and bromine, and these were connected with oxygen through experiments upon chlorates and bromates. Our whole system of atomic weights, with only a few exceptions, is based to-day upon the analyses of several oxyhalogen salts. Their accuracy is assumed, and all anomalies which appear in determinations based upon other lines of research are commonly ascribed to undiscovered errors. The assumption may be sustained, but it is not yet beyond the reach of criticism.

Consider, for example, the well known ratio $\text{Ag} : \text{AgNO}_3 = 100 : 157.149$. If $\text{Ag} = 107.93$, as determined through the analyses of chlorates and bromates, then $\text{N} = 14.037$, or 14.04 as given in our table. If, on the other hand, $\text{N} = 14.009$, as given by Guye, Ag becomes 107.881 . The difference between the two values for silver evidently represents a difference in our methods of connecting the element with oxygen, the latter being taken as the standard. For each method strong arguments are possible, and for each value other corroborative testimony can be cited. Neither procedure is wholly free from objections, and the final conclusion, therefore, is one of uncertainty. We cannot safely reject either line of evidence, nor can we accept one as surely more exact than the other. Concordant values for silver can be derived from either method of discussion, as Guye has shown, and through them the entire system of atomic weights is affected.

In this condition of affairs, the position of the Committee can only be one of conservatism. It is better to retain the table we have until at least some of the doubts which now affect it have been eliminated. It seems to be essential that the foundations of the atomic weight table should be both broadened and strengthened, and that new lines of research connecting the fundamental values with oxygen shall be investigated. Some work of this kind is already promised from the laboratory of Harvard University, to be carried out by Richards and his colleagues, but that need

not exclude other activities. It is to be hoped that a number of investigators may take up the consideration of this problem, and that the methods of attack upon it may be multiplied. The careful study of such salts as the sulphates, carbonates, and nitrates might perhaps be profitable. Whether the organic salts of silver could be utilised for good atomic weight determinations is still uncertain.

F. W. CLARKE.
HENRI MOISSAN.
KARL SEUBERT.
T. E. THORPE.

International Atomic Weights. (1906).

					O=16.
Aluminium	..	..	..	Al	27.1
Antimony	..	..	..	Sb	120.2
Argon	..	..	..	A	39.9
Arsenic	..	..	..	As	75.0
Barium	..	..	..	Ba	137.4
Bismuth	..	..	..	Bi	208.5
Boron	..	..	..	B	11
Bromine	..	..	..	Br	79.96
Cadmium	..	..	..	Cd	112.4
Cæsium	..	..	..	Cs	132.9
Calcium	..	..	..	Ca	40.1
Carbon	..	..	..	C	12.00
Cerium	..	..	..	Ce	140.25
Chlorine	..	..	..	Cl	35.45
Chromium	..	..	..	Cr	52.1
Cobalt	..	..	..	Co	59.0
Columbium	..	..	..	Cb	94
Copper	..	..	..	Cu	63.6
Erbium	..	..	..	Er	166
Fluorine	..	..	..	F	19
Gadolinium	..	..	..	Gd	156
Gallium	..	..	..	Ga	70
Germanium	..	..	..	Ge	72.5
Glucinum	..	..	..	Gl	9.1
Gold	..	..	..	Au	197.2
Helium	..	..	..	He	4
Hydrogen	..	..	..	H	1.008
Indium	..	..	..	In	115
Iodine	..	..	..	I	126.97
Iridium	..	..	..	Ir	193.0
Iron	..	..	..	Fe	55.9
Krypton	..	..	..	Kr	81.8
Lanthanum	..	..	..	La	138.9
Lead	..	..	..	Pb	206.9
Lithium	..	..	..	Li	7.03
Magnesium	..	..	..	Mg	24.36
Manganese	..	..	..	Mn	55.0
Mercury	..	..	..	Hg	200.0
Molybdenum	..	..	..	Mo	96.0
Neodymium	..	..	..	Nd	143.6
Neon	..	..	..	Ne	20
Nickel	..	..	..	Ni	58.7
Nitrogen	..	..	..	N	14.04
Osmium	..	..	..	Os	191
Oxygen	..	..	..	O	16.00
Palladium	..	..	..	Pd	106.5
Phosphorus	..	..	..	P	31.0
Platinum	..	..	..	Pt	194.8
Potassium	..	..	..	K	39.15
Praseodymium	..	..	..	Pr	140.5
Radium	..	..	..	Rd	225
Rhodium	..	..	..	Rh	103.0
Rubidium	..	..	..	Rb	85.5
Ruthenium	..	..	..	Ru	101.7
Samarium	..	..	..	Sm	150.3
Scandium	..	..	..	Sc	44.1
Selenium	..	..	..	Se	79.2
Silicon	..	..	..	Si	28.4
Silver	..	..	..	Ag	107.93
Sodium	..	..	..	Na	23.05
Strontium	..	..	..	Sr	87.6

		O=16.
Sulphur	S	32.06
Tantalum	Ta	183
Tellurium	Te	127.6
Terbium	Tb	160
Thallium	Tl	204.1
Thorium	Th	232.5
Thulium	Tm	171
Tin	Sn	119.0
Titanium	Ti	48.1
Tungsten	W	184
Uranium	U	238.5
Vanadium	V	51.2
Xenon	Xe	128
Ytterbium	Yb	173.0
Yttrium	Yt	89.0
Zinc	Zn	65.4
Zirconium	Zr	90.6

NOTICES OF BOOKS.

Finite and Infinite. By THOMAS CURRAN RYAN. Philadelphia and London: J. B. Lippincott Company. 1905.

THE author of this work, like so many who make a hobby of science or philosophy without devoting all their energies to it, discusses his subject with great heat and verbosity, although he does not show that he has mastered the essentials of these branches of knowledge. This is specially noticeable in the second part of the book, in which an endeavour is made to prove that the universe is finite—a good many facts and arguments being brought forward to demonstrate also that the sky is matter of some sort beyond the stars. The author expresses considerable surprise that the editor of "Popular Astronomy," to whom he had entrusted an article containing an exposition of his theories, did not make use of it; but it may be suggested that possibly an explanation is to be found in the fact that these views, when original, are hardly satisfactorily established in his work. The first part of the book discusses Idealistic Pantheism, with special reference to Fiske's writings, which are criticised at some length, the object being to warn the Christian world of the danger threatened to it by Idealism.

Investigations of Infra-red Spectra. By WILLIAM W. COBLENTZ. Washington, D.C.: The Carnegie Institution of Washington. 1905.

THIS work gives a most complete account of the systematic investigation of infra-red spectra, begun by the author when a student at Cornell University and continued at the Carnegie Institution of Washington. Part I. of the book deals with the Infra-red Absorption Spectra, and describes researches undertaken for the purpose of determining the effect of molecular weight upon absorption spectra. After an explanation of the method and apparatus employed, the results obtained with at least 130 compounds of carbon and hydrogen, the spectra of which were explored in the majority of cases to 14μ or 15μ , are described, and a general discussion of the whole work draws attention to various important conclusions which may be drawn from it. This part of the book also contains many tables of line spectra, besides transmission curves. Part II. gives a record of a research on the Infra-red Emission Spectra, the object of the work being the study of the region lying beyond 2μ . This section is comparatively short, and consists chiefly of an account of experimental observations, although some theoretical points are briefly discussed. The whole book is most interesting, and spectroscopists will find that it well deserves careful reading.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

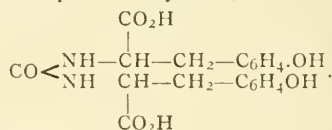
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 1, January 2, 1906.

Estimation of Carbonic Oxide in the Air by means of Iodic Anhydride.—Armand Gautier.—The author adds as a note to Jaubert's paper in the last number that as long ago as 1898 he noticed that the method of estimating the carbonic oxide in the air by means of iodic anhydride, contains an error due to the fact of the reaction of the latter substance on acetylene. He also gave a means of correcting the error. He states, however, that acetylene is not present in appreciable quantities in ordinary town air.

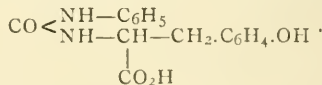
Determination of Rare Gases in Natural Gaseous Mixtures.—Charles Moureu.—The author describes with drawing the apparatus he is using in a series of researches on the determination of rare gases in natural gaseous mixtures.

Heat of Fusion of Ice.—A. Leduc.—The author re-determines the heat of fusion of ice, and after careful experiments and calculation finds the specific mass of ice at 0° to be 0.9176 instead of 0.91674 as determined by Bunsen. From this the heat of fusion of ice is found to be 79.2 calories at 15° .

Synthetic Union of the Amide Acids Derived from the Albumines.—L. Hugounenq and A. Morel.—The authors' researches on the synthetic union of the amide acids derived from the albumines were made on tyrosine, which is with leucine one of the most important products of the decomposition of albumenoid bodies. The researches lead to the following results:—1. Below 100° carbon oxychloride has no action on tyrosine. At about 150° in a sealed tube the reaction is accompanied by the formation of tarry products. 2. In the cold, COCl_2 acts on the sodium salt of tyrosine dissolved in water, giving a symmetric urea product of tyrosine,—



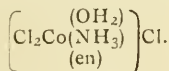
The carbimides react on tyrosine dissolved in alkaline water, giving rise to mixed urea products of tyrosine and amines, and so leading to the preparation of mixed urates of the two different amide acids. As an example, the author prepares the mixed urea product of tyrosine and aniline,—



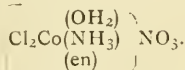
Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 17, 1905.

Mixed Triamine Cobalt Salts containing Ethylene Diamine and Ammonia.—A. Werner and A. Grün.—The investigation of some members of the triamine cobalt series containing ethylene diamine has shown that the presence of ethylene diamine alters the chemical and physical properties of the triamine salts more than is the case with tetramine salts, and that, in contrast to the behaviour of the tetramine salts, the stability of the cobaltic radical of the triamine salts is not raised but

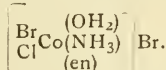
lowered by the presence of ethylene diamine. Trinitro ethylene diamine triamine cobalt, formed by the action of ethylene diamine on the tetranitro diamine cobalt acid salt, is converted by boiling hydrochloric acid into a black salt, which, on re-crystallisation from water containing hydrochloric acid, gives greenish black needles of composition:—



Only one chlorine atom of this salt is replaced in the usual way; thus when nitric acid acts upon it the following nitrate is formed:—



In aqueous solution one intra radical chlorine atom, in consequence of hydration, suffers a very rapid electrolytic dissociation, so that the green solution turns blue. This blue solution yields olive-green needles when hydrobromic acid is added, and the compound thus formed has the formula—

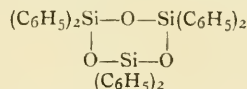


These transformations show that the presence of ethylene diamine in the triamine cobalt radical increases the mobility of the acid residues combined with the cobalt, so that the internal stability of the complex cobalt radicals in the form of salts is much less than that of the ordinary triamine salts.

Perchromic Acid Anhydride Triamine.—E. H. Riesenfeld.—Hofmann and Hiendlmaier (*Berichte*, 1905, xxxviii., 3059; *CHEMICAL NEWS*, 1905, xcii., 201) think that when chromate is oxidised by hydrogen peroxide the composition of the product varies according to the amount of ammonia present in the solution. The author's experiments, however, show that whether the ammonium chromate solution contains only 2.5 per cent free ammonia, or is saturated with ammonia, an ammonium perchromate of the formula $(\text{NH}_4)_3\text{CrO}_8$ is obtained, provided that the solution contains a sufficient quantity of hydrogen peroxide (3 to 5 per cent), and that it is not warmed above 0° until all the salt has completely crystallised out. The form of the crystals, however, is dependent upon the amount of ammonia present. If the solution contains only small amounts of ammonia, octohedric pyramids are obtained, and when large amounts of ammonia are present the crystals which separate out are identical with those which Hofmann and Hiendlmaier obtained as impurities in the preparation of perchromic acid anhydride triamine. If the solution contains an insufficient amount of hydrogen peroxide, or is warmed above 0° , either a mixture of $(\text{NH}_4)_3\text{CrO}_8$ and $\text{CrO}_4 \cdot 3\text{NH}_3$ is obtained, or else the latter only. This is due to the fact that perchromic acid anhydride triamine is much more stable than ammonium perchromate. Perchromic acid anhydride triamine is known in the form of needles and plates, and Hofmann and Hiendlmaier thought that these were two isomeric substances. Crystallographic examination, however, shows that they are not isomeric forms, but are probably identical. When the triamine is decomposed by means of acids chromic peroxide is not formed, but a mixture of chromium oxide and hydrogen peroxide.

Diphenyl Silicon Oxide and Benzyl Silicon Compounds.—W. Dilthey.—By the action of phenyl magnesium bromide on silicon tetrachloride in ethereal solution mono-, di-, or tri-phenyl silicon compounds are formed, according to the amount of magnesium compound used. It has not yet been found possible to replace the fourth atom of chlorine by the phenyl group. Diphenyl silicon hydroxide, $(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$, on being fused yields diphenyl silicon oxide, $(\text{C}_6\text{H}_5)_2\text{SiO}$. The latter forms a gelatinous

mass, but may be obtained in crystalline form (melting at 188°) by adding a drop of acetic acid anhydride to the gelatine, when the whole mass instantly crystallises. The determination of the molecular weight of the crystals cryoscopically in alcohol showed that the formula $(\text{C}_6\text{H}_5)_2\text{SiO}$ must be trebled, while approximately the same result was obtained from the gelatine in benzene. As diphenyl silicon hydroxide, $(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$, is monomolecular, evidently at first the gelatine is monomolecular, but is immediately transformed to the trimolecular form, which then crystallises. This behaviour recalls the frequently occurring polymerisation phenomena which have been observed with carbon non-metallic compounds. The constitutional formula is—



Diphenyl silicon oxide is the first substance (as far as the author knows) in which the power of polymerisation has been experimentally demonstrated, although the constitutional formulæ which have been adopted for the silicates have illustrated the same great tendency to form condensed molecules.

Electrolytic Reduction of Carbonic Acid.—R. Ehrenfeld.—It has been shown that when cold saturated potassium sulphate solutions are electrolysed with a low current density, a current of carbon dioxide being steadily led through them, formic acid appears in the cathode liquid, and it is the HCO_3 ion which undergoes the reduction. The author has electrolysed ammonium carbonate solutions, and examined the reduction products resulting at the amalgamated zinc cathode. He finds that when the cathode liquid is distilled in a current of steam, formic acid can be detected in the distillate. No reduction occurs when the cathode is iron, platinum, copper, lead, or nickel. If either the concentration of the ammonium carbonate solution or the current density sinks below a certain minimum no reduction occurs. It is the NH_4CO_3 ion which is reduced at the cathode, for formic acid is formed when solutions of ammonium carbonate containing large amounts of ammonia are electrolysed. A difficulty arises, however, when it is observed that no formic acid is formed when cold saturated sodium carbonate solutions are electrolysed, but it may be that other factors condition the electrolytic formation of formic acid from salts of CO_2 although the HCO_3 ion is at the basis of the reduction.

MEETINGS FOR THE WEEK.

- MONDAY, 5th.—Society of Arts, 8. (Cantor Lectures). "Modern Warships," by Sir William White, F.R.S., &c.
— Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 7. "Loss of Nitre in the Chamber Process" (Part II.), by J. K. H. Inglis.
- TUESDAY, 6th.—Royal Institution, 5. "Food and Nutrition," by Prof. William Stirling, M.D., &c.
— Society of Arts, 4.30. "Imperial Immigration," by Octavius Charles Beale.
- WEDNESDAY, 7th.—Society of Arts, 8. "Progress in Electric Lighting," by Leon Gaster.
— Society of Public Analysts, 8. (Annual Meeting). President's Address. "Note on Dutch Cheese," by C. H. Cribb. "Assay of Mercury ores," by G. T. Holloway. "Purification of Zinc and Hydrochloric Acid," by L. T. Thorne and E. H. Jeffers. "The Facing of Rice," by C. H. Cribb and P. A. E. Richards.
- THURSDAY, 8th.—Royal Institution, 5. "The Significance of the Future in the Theory of Evolution," by Benjamin Kidd.
- FRIDAY, 9th.—Royal Institution, 9. "Eclipse Problems and Observations," by Hugh Frank Newall, F.R.S., &c.
— Physical 8. (Annual General Meeting). Address by Prof. Perry, President-Elect.
- SATURDAY, 10th.—Royal Institution, 3. "Advances in Microscopy," by John W. Gordon.

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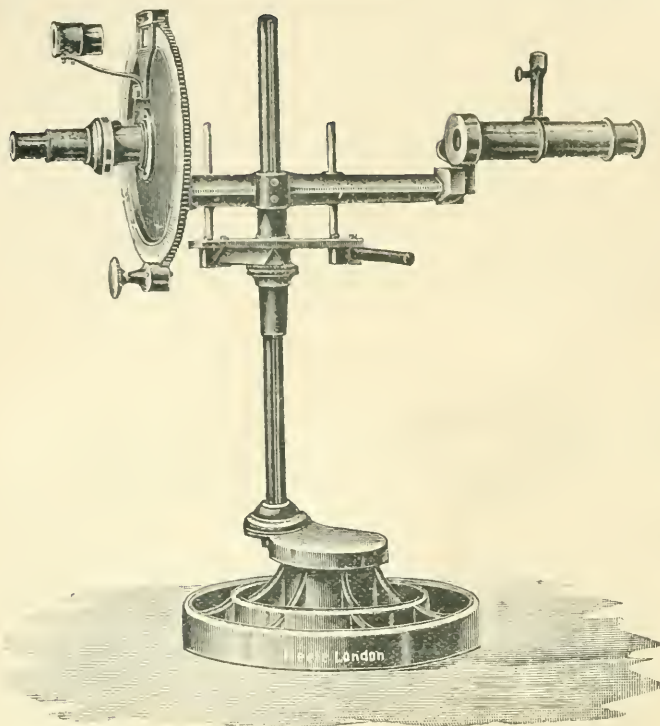
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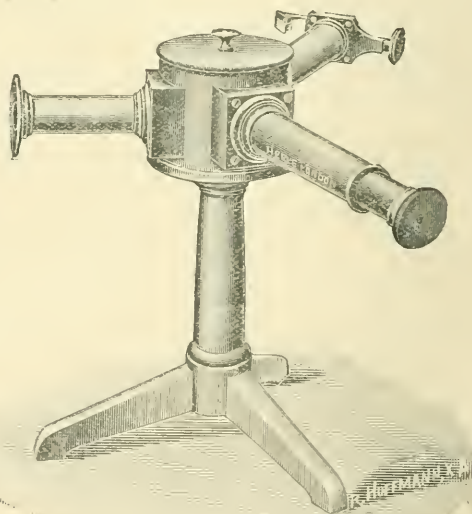
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VOL. XCIII., No. 2411.

THE INTERACTION OF HYDROCHLORIC ACID AND POTASSIUM PERMANGANATE IN THE PRESENCE OF FERRIC CHLORIDE.*

By JAMES BROWN.

LÖWENTHAL (*Zeit. Anal. Chem.*, i., 329) and Lenssen were the first to show that the titration of ferrous salts by potassium permanganate in the presence of hydrochloric acid, as proposed by Margueritte (*Ann. Chim.*, [3], xviii., 244), does not admit of quantitative accuracy because of the evolution of chlorine by the interaction of hydrochloric acid and potassium permanganate, and to propose as a remedy for this source of error the titration of successive equal portions of the ferrous salt to be determined until the readings become constant.

This tendency toward evolution of chlorine in titrations of a ferrous salt by potassium permanganate in the presence of hydrochloric acid, as compared with the alleged absence of such tendency in similar titrations of oxalic acid, was explained by Zimmermann on the supposition that the oxidation of the iron proceeds so rapidly as to form oxides of iron higher than the sesquioxide, which then react to oxidise more iron and liberate chlorine from hydrochloric acid (*Ann. Chem.*, ccxiii., 311). Quite recently Wagner explains this phenomenon by the assumed formation of chlor-ferrous acid (analogous to chlor-platinic and chlor-aureic acids), which is more easily oxidised by the permanganate than is hydrochloric acid under similar conditions ("Maassanalytische Studien, Habilitationsschrift," Leipzig, 1898). Recent work has shown that there is a slight though real waste of permanganate in titrations of oxalic acid under the conditions named, and that this loss is proportional to the amount of hydrochloric acid present (Gooch and Peters, *Am. Journ. Sci.*, [4], vol. vii., 463). It still appears, however, that this loss is greater in titrations of ferrous salts than in those of oxalic acid under the conditions named.

Wagner's work in relation to the phenomenon mentioned above has been reviewed very carefully, and it has been found that, although as shown by him more permanganate is required to bring about final coloration against equal quantities of oxalic acid in experiments in which equal quantities of potassium permanganate are digested with a constant quantity of normal hydrochloric acid and a measured volume of tenth normal ferric chloride, than when an equivalent quantity of tenth-normal hydrochloric acid is substituted for the tenth-normal ferric chloride, the differences vary within wide limits and disappear entirely if the chlorine formed by the interaction of the potassium permanganate and hydrochloric acid is removed during the digestion. When also the chlorine is thus removed the same quantity of permanganate is required to bring about final coloration, whether ferric chloride is present or not. It is found also that the permanganate is entirely destroyed within the limits proposed by Wagner, and that after an hour's digestion, and in fact long before, the permanganate colour has entirely disappeared and only the hydrated oxides of manganese—formed according to the Guyard reaction—are visible in the digestion liquid.

Wagner describes no special form of apparatus in his work, and gives no details as to size of flask used to contain the digestion liquids, form of bath, &c., pointing out the fact simply that he used a return-condenser 60 c.m. in

length. It was found convenient in the experiments about to be described to use a 250 c.c. flask to contain the solutions during digestion, and to heat the solutions in an Ostwald thermostat.

The experiments of Table I. were conducted, as outlined by Wagner, in the following manner:—To a 250 c.c. flask were added 100 c.c. of normal hydrochloric acid (that is, a solution containing 36.4575 grms. of the acid to the litre), and in addition either 9.91 c.c. of tenth-normal hydrochloric acid (prepared by diluting 100 c.c. of the normal solution to one litre) or 9.91 c.c. of tenth normal ferric chloride. Of approximately twentieth normal potassium permanganate, carefully standardised against ammonium oxalate, 9.91 c.c. were then added, and the flask, fitted in a ground joint to a return-condenser 60 c.m. in length and with a bore approximately 3 c.m. in diameter, was heated for one hour in the Ostwald thermostat at a temperature of 50° C. Of tenth normal oxalic acid, 9.91 c.c. were then added to the digestion liquid and a measured volume of the same permanganate solution as was added before digestion was run in to colour. The difference between the total permanganate used (that is, the permanganate added before digestion plus that added to bring about final coloration against the oxalic acid) and the permanganate equivalent of the oxalic acid added, gives, according to Wagner, the permanganate reduced during the digestion. The results of these experiments are recorded in Table I.

Here it may be seen that although in general more permanganate is required to bring about final coloration in those experiments in which ferric chloride was used than in its absence, the results show at best wide variation among themselves, and the amounts of permanganate apparently destroyed during the digestion are at all events considerably greater than in the experiments conducted by Wagner under similar conditions. In the experiments recorded in Table I., in the average 4.73 c.c. of permanganate were apparently destroyed where ferric chloride was not used, and 5.37 c.c. in the presence of ferric chloride; while in Wagner's experiments 0.96 c.c. of permanganate was apparently reduced without use of ferric chloride and 1.41 c.c. in its presence.

Since, as has been noted above, the permanganate colour entirely disappeared in the experiments of Table I. long before the termination of the hour's digestion, while only small amounts of hydrated oxides of manganese varying in colour from brown to black were visible in the digestion liquid, it seemed probable that more permanganate was really reduced during the digestion than is indicated in these experiments. Moreover, a strong odour of chlorine was noticeable in these experiments, and it seemed probable that some of the chlorine, formed by the interaction of the potassium permanganate and hydrochloric acid during the digestion, remained to take part in the oxidation of the oxalic acid introduced, and that, therefore, on running in permanganate solution to colour, less of the latter was required than corresponded to the oxalic acid left unoxidised by the residual oxides of manganese. It was therefore decided to remove if possible this chlorine, and to this end a vigorous current of carbon dioxide or air was passed through the digestion liquid while heating. In this way the chlorine was readily removed and starch and potassium iodide paper held in the current of carbon dioxide or air gave no test for chlorine.

The experiments of Table II., in which no ferric chloride was used, were conducted precisely as were those of Table I., except that a vigorous current of carbon dioxide generated in a Kipp generator by action of hydrochloric acid on marble, and washed and dried by passing first through a bottle filled with water and then through a calcium chloride tube, was passed through the liquid during the process of digestion. Because also of the greater ease of measuring out accurately 9.90 c.c. rather than the 9.91 c.c. used by Wagner and in the experiments of Table I., the former volume of reagents was substituted for the latter in the experiments to follow. It will readily be

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, xix., January, 1905.

TABLE I.
(Temperature, 50° C.; Time of Digestion, Sixty Minutes).
9.91 c.c. $\text{H}_2\text{C}_2\text{O}_4$ = 20.25 c.c. KMnO_4 .

N/1 HCl. C.c.	N/10 HCl. C.c.	N/10 FeCl_3 . C.c.	KMnO_4 before digestion. C.c.	N/10 $\text{H}_2\text{C}_2\text{O}_4$. C.c.	KMnO_4 to colour. C.c.	KMnO_4 apparently reduced during digestion. C.c.
100	9.91	—	9.91	9.91	15.89	5.55
100	9.91	—	9.91	9.91	15.11	4.77
100	9.91	—	9.91	9.91	15.15	4.81
100	9.91	—	9.91	9.91	15.07	4.73
100	9.91	—	9.91	9.91	15.13	4.79
100	9.91	—	9.91	9.91	15.07	4.73
100	9.91	—	9.91	9.91	15.08	4.74
100	9.91	—	9.91	9.91	15.02	4.68
100	9.91	—	9.91	9.91	14.85	4.51
100	9.91	—	9.91	9.91	14.40	4.06
100	9.91	—	9.91	9.91	15.05	4.71
100	—	9.91	9.91	9.91	15.60	5.26
100	—	9.91	9.91	9.91	15.35	5.01
100	—	9.91	9.91	9.91	15.32	4.98
100	—	9.91	9.91	9.91	15.88	5.54
100	—	9.91	9.91	9.91	15.42	5.08
100	—	9.91	9.91	9.91	15.45	5.11
100	—	9.91	9.91	9.91	15.95	5.61
100	—	9.91	9.91	9.91	15.41	5.07
100	—	9.91	9.91	9.91	15.95	5.61
100	—	9.91	9.91	9.91	15.65	6.31
100	—	9.91	9.91	9.91	15.75	5.41
100	—	9.91	9.91	9.91	15.79	5.45

TABLE II.
(Temperature, 50° C.; Time of Digestion, Sixty Minutes).

	N/1 HCl. C.c.	N/10 HCl. C.c.	KMnO_4 before digestion. C.c.	$\text{H}_2\text{C}_2\text{O}_4$. C.c.	KMnO_4 to colour. C.c.	KMnO_4 apparently reduced during digestion. C.c.
9.90 c.c. approximately N/10 $\text{H}_2\text{C}_2\text{O}_4$ = 23.52 c.c. KMnO_4 .						
I.	100	9.90	9.90	9.90	22.19	8.57
II.	100	9.90	9.90	9.90	22.10	8.48
III.	100	9.90	9.90	9.90	22.15	8.53
IV.	100	9.90	9.90	9.90	22.11	8.49
9.90 c.c. approximately N/10 $\text{H}_2\text{C}_2\text{O}_4$ = 23.65 c.c. KMnO_4 .						
V.	100	9.90	9.90	9.90	22.15	8.40
VI.	100	9.90	9.90	9.90	21.79	8.04
VII.	100	9.90	9.90	9.90	22.24	8.49
VIII.	100	9.90	9.90	9.90	22.21	8.46
IX.	100	9.90	9.90	9.90	22.24	8.49
X.	100	9.90	9.90	9.90	22.23	8.48
XI.	100	9.90	9.90	9.90	22.25	8.50
XII.	100	9.00	9.90	9.90	22.15	8.40
XIII.	100	9.90	19.80	9.90	19.77	15.92
XIV.	100	9.90	19.80	9.90	19.83	15.98
XV.	100	9.90	50.0	25.00	44.53	34.81
XVI.	100	9.90	50.0	25.00	44.47	34.75
XVII.	100	9.90	50.0	25.00	44.44	34.72
XVIII.	100	9.90	50.0	25.00	44.58	34.86

seen that in the case of tenth normal hydrochloric acid 0.01 c.c. is negligible as compared with the large amount of hydrochloric acid used in the experiments.

The results of these experiments are recorded in Table II.

From these results the conclusion may be drawn that the low indications of the amount of permanganate apparently reduced during digestion in the experiments recorded in Table I., at least so far as concerns those experiments in which no ferric chloride was used, were in all probability due to the oxidising action of the unexpelled chlorine on the oxalic acid, and that the large variations in results were due to the greater or less retention of the chlorine. In Experiments XIII. to XVIII. it is seen further that amounts

of permanganate very much greater than those used in Wagner's experiments and in the experiments of Table I. can be reduced by the same amount of hydrochloric acid, and under the same conditions of temperature and time as in those other experiments; for, in these last experiments, also, the permanganate colour entirely disappeared during the digestion.

In order to ascertain if a current of air is equally as effective in removing the chlorine as is carbon dioxide, and also because of the greater availability of the former, the experiments recorded in Table III. were conducted in a manner identical with those of Table II., except that a current of air dried and purified was substituted for the carbon dioxide. When also the success of the air current

TABLE III.
 (Temperature, 50° C.).
 9.90 c.c. approximately N/10 $\text{H}_2\text{C}_2\text{O}_4$ = 20.09 c.c. KMnO_4 .

	N/1 HCl.	N/10 HCl.	N/10 FeCl_3 .	KMnO_4 before digestion.	Time of digestion.	Residual KMnO_4 colour after digestion.	Cl test after digestion.	$\text{H}_2\text{C}_2\text{O}_4$.	KMnO_4 to colour.	KMnO_4 apparently reduced during digestion.
	C.c.	C.c.	C.c.	C.c.	Mins.			C.c.	C.c.	C.c.
I.	100	9.90	—	9.90	60	None	None	9.90	18.88	8.69
II.	100	9.90	—	9.90	60	"	"	9.90	18.87	8.68
III.	100	9.90	—	9.90	60	"	"	9.90	18.80	8.61
IV.	100	9.90	—	9.90	60	"	"	9.90	18.81	8.62
V.	100	9.90	—	9.90	60	"	"	9.90	18.80	8.61
VI.	100	9.90	—	9.90	60	"	"	9.90	18.82	8.63
VII.	100	9.90	—	9.90	30	"	"	9.90	18.77	8.58
VIII.	100	9.90	—	9.90	30	"	Doubtful	9.00	18.70	8.51
IX.	100	9.90	—	9.90	15	"	Very faint	9.90	18.70	8.51
X.	100	9.90	—	9.90	15	"	"	9.90	18.68	8.49
XI.	100	—	9.90	9.90	60	"	None	9.90	18.87	8.68
XII.	100	—	9.90	9.90	60	"	"	9.90	18.85	8.66
XIII.	100	—	9.90	9.90	60	"	"	9.90	18.81	8.62
XIV.	100	—	9.90	9.90	60	"	"	9.90	18.81	8.62
XV.	100	—	9.90	9.90	60	"	"	9.90	18.87	8.68
XVI.	100	—	9.90	9.90	60	"	"	9.99	18.85	8.66
XVII.	100	—	9.90	9.90	30	"	"	9.90	18.80	8.61
XVIII.	100	—	9.90	9.90	30	"	Doubtful	9.90	18.72	8.53
XIX.	100	—	9.90	9.90	15	"	Very faint	9.90	18.65	8.46
XX.	100	—	9.90	9.90	15	"	"	9.90	18.67	8.48

TABLE IV.
 (Temperature, 50° C.).

	N/1 HCl.	N/10 HCl.	KMnO_4 before digestion.	H_2O .	Volume during digestion.	Time of digestion.	Residual KMnO_4 colour after digestion.	Cl test after digestion.	$\text{H}_2\text{C}_2\text{O}_4$.	KMnO_4 to colour.	KMnO_4 apparently reduced during digestion.
	C.c.	C.c.	C.c.	C.c.	C.c.	Mins.			C.c.	C.c.	C.c.
40 c.c. N/10 $(\text{H}_4\text{N})_2\text{C}_2\text{O}_4$ = 37.64 c.c. KMnO_4 ; 100 c.c. $\text{H}_2\text{C}_2\text{O}_4$ = 101.40 c.c. KMnO_4 .											
I.	100	9.90	100	—	210	60	None	Faint	100	59.52	58.12
II.	100	9.90	100	—	210	60	"	"	100	58.44	57.04
40 c.c. N/10 $(\text{H}_4\text{N})_2\text{C}_2\text{O}_4$ = 18.35 c.c. KMnO_4 ; 50 c.c. N/5 $\text{H}_2\text{C}_2\text{O}_4$ = 49.26 c.c. KMnO_4 .											
III.	100	9.90	50	—	160	60	None	None	50	30.72	31.46
IV.	100	9.90	50	—	160	60	"	"	50	30.75	31.49
V.	100	9.90	50	—	160	60	"	"	50	30.76	31.50
VI.	100	9.90	50	—	160	60	"	"	50	30.78	31.52
VII.	100	9.90	50	—	160	60	"	"	50	30.88	31.62
VIII.	100	9.90	50	50	210	60	Faint	Faint	50	27.11	27.85
IX.	100	9.90	50	50	210	60	"	"	50	27.92	28.66
X.	100	9.90	50	50	210	60	"	"	50	28.52	29.26
XI.	100	9.90	50	50	210	60	"	"	50	28.54	29.28
XII.	100	9.90	50	50	210	60	"	"	50	29.14	29.88
XIII.	100	9.90	50	50	210	60	"	"	50	28.98	29.72
XIV.	100	9.90	50	50	210	60	"	"	50	28.56	29.30
XV.	100	9.90	50	50	210	60	"	"	50	29.96	30.70
XVI.	100	9.90	50	50	210	85	None	Very faint	50	29.96	30.70
XVII.	100	9.90	50	50	210	60	Faint	Faint	50	30.22	30.96
XVIII.	100	9.90	75	—	185	60	None	Marked	50	20.72	46.46
XIX.	100	9.90	50	50	210	120	"	None	50	30.31	31.05
XX.	100	9.90	100	—	210	60	Marked	Marked	60	19.58	60.47
XXI.	100	9.90	75	50	235	220	None	Faint	50	21.84	47.58
XXII.	100	9.90	100	50	260	180	Marked	Marked	60	10.18	51.07
2N/1 HCl.											
XXIII.	50	9.90	50	—	110	60	None	Faint	50	30.23	30.97
XXIV.	50	9.90	75	—	135	60	"	Marked	—	—	—
XXV.	50	9.90	75	—	135	60	"	"	50	30.69	56.43

was apparent, ferric chloride was again used and the effect noted.

Results are outlined in Table III.

Here again may be noted the concordance of results when the chlorine is all removed before the addition of oxalic acid, as well as the fact that under these conditions substantially the same amount of permanganate is required

to bring about the end reaction, whether ferric chloride is present or not; and that consequently as much permanganate is reduced during the digestion in the latter case as in the former. Also by a comparison of Experiments VIII.—X. and XVIII.—XX., in which a slight trace of chlorine remained, with Experiments I.—VI. and XI.—XVI., in which the chlorine was entirely removed,

we again see the oxidising effect of the residual chlorine on the oxalic acid; for even in the former sets of experiments, in which the digestion was carried on only fifteen or thirty minutes, the permanganate colour had entirely disappeared at the end of the digestion. The variations in the amount of permanganate apparently reduced during the digestion in the experiments recorded in Table I. are, therefore, doubtless due to the interfering action of the residual chlorine held in solution. The " KMnO_4 apparently reduced during digestion" in the experiments of Table II., and in those of Table III. in which the chlorine was entirely removed during the digestion, represents the amounts of permanganate entirely reduced to manganous chloride, while the differences between these amounts and the " KMnO_4 before digestion" represent the residual oxides of manganese. Similar differences in the experiments of Table I., and in those of Table III. in which the chlorine was only partially removed, represent the residual oxides of manganese and the chlorine retained in solution.

The amount of chlorine held in solution when no means are employed to remove it, depends largely on the form and size of the flask used to contain the solutions during digestion, also on the dimensions of the return-condenser, and will vary according to the greater or less amount of shaking to which the flask is subjected during the entire course of the experiment. It is, therefore, evident that Wagner's experiments are in no way indicative of the relative amounts of potassium permanganate reduced in the presence or absence of ferric chloride, other conditions being constant, but are an indication simply of the greater or less retention of chlorine in solution in the form of apparatus used by him; for it has been shown that in all experiments conducted within the limits proposed by Wagner the permanganate is entirely destroyed, and that any variations in the amount of permanganate apparently destroyed during digestion disappear when the chlorine is entirely removed from the sphere of action. The possibility of any interfering action of ferric chloride in titrations of oxalic acid by potassium permanganate is excluded by the results of the experiments of Table III., in which we find no variations in results whether ferric chloride is present or not. The cause of the apparently greater destruction of potassium permanganate in those experiments of Table I. in which ferric chloride was used than in those in which ferric chloride was not used, is now under investigation.

Since in all experiments thus far conducted the permanganate colour has been entirely destroyed, the experiments of Table IV. were made to ascertain if possible how much permanganate can be destroyed by the amount of hydrochloric acid used in the experiments of Tables I., II., and III. under the same conditions of time and temperature, and also during greater periods of time. It will readily be seen from the evident oxidation of oxalic acid by chlorine in previous experiments that an exact measure of the maximum amount of permanganate reduction during a given period of time can be obtained only when all the chlorine is removed and at the same time the permanganate colour just disappears—a condition difficult to attain. The results recorded in Table IV. should therefore be regarded as approximate only.

Thus it may be seen that the same amount of hydrochloric acid as was used in the experiments of Tables I., II., and III. is capable of breaking down approximately thirty times as much permanganate as was used in those experiments and in the experiments of Wagner, conditions of time and temperature being the same. Changes of volume are of course involved in the use of varying amounts of permanganate, but an increase in volume would in all probability be attended by a decrease in the relative amount of permanganate reduced by a constant quantity of hydrochloric acid. In any case, the results show a more extensive reduction than is indicated in Wagner's experiments and in those of Tables I., II., and III.

The conclusion must be drawn, then, that Wagner's experiments in no way show the catalytic effect of ferric chloride in the interaction between hydrochloric acid and potassium permanganate, nor do they furnish evidence in support of the assumed formation of chlor-ferrous acid. They afford simply an indication of the greater or less retention of chlorine in solution, and the greater or less oxidising action of this chlorine on the oxalic acid in the presence or absence of ferric chloride.

The author is indebted to Prof. F. A. Gooch for much advice and assistance in the preparation of this paper.

A CONVENIENT APPARATUS FOR DETERMINING VOLATILE SUBSTANCES BY LOSS OF WEIGHT.*

By J. LEHN KREIDER.

Of the various forms of apparatus designed for the determination of volatile products of reactions, some are cumbersome, and many require for their construction skill in glass-blowing. The apparatus here described is light



and easily made from three test-tubes, modified and fitted as shown in the figure. The test-tube, A, is changed in no way from its original form; B is perforated, in the bottom, with a hole about 1 c.m. in diameter, and fits tightly within A; and C, so selected that it fits loosely within B, is drawn out to a small capillary tube.

When the apparatus is to be used, the capillary of C is pushed through the hole of B, packed loosely with cotton; B is filled to the depth of from 6 c.m. to 8 c.m. (about two-thirds of its contents), with granular calcium chloride; and B and C are adjusted as shown.

To the test-tube, C, is fitted a one-holed stopper, through which passes a short glass tube which is to be closed by a rubber cap and plug. Upon removing the plug, and applying suction to the short tube, the reagent employed to liberate the volatile product to be determined is drawn up through this capillary until C is sufficiently filled. Upon replacing the plug the reagent remains within C, held by atmospheric pressure.

The tubes A and B may be so selected that very little of the product evolved can escape between them, but in case they fit very loosely, a ring of paraffin melted into the mouth of A, about B, by means of a hot iron or wire, seals the joint securely. A very convenient way to attach the paraffin is to melt it between A and another tube, which fits A, as does B, and may be removed by a turning motion, leaving the ring into which B will fit, and which then requires very little heating to make a tight joint. If care be used in taking apart A and B, at the close of an experiment, such a ring of paraffin remains in place, and may be used many times without replacement, being re-melted by a touch of the hot wire before every new experiment.

In making a determination, the substance under examination is weighed and placed in the bottom of A. The reagent to be employed, 10 c.m.³ to 15 c.m.³, is drawn into C, and held there in the manner described. The test-tube A is slipped over B, and this joint is sealed with paraffin, as has been shown. The apparatus is wiped, placed on the balance, and weighed.

Upon removing the cap from the small tube in C, the reagent runs from C into A. The volatile product is formed, is forced upward through the drying column of calcium chloride, and escapes through the annular space between

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, 1905, xix., p. 188.

B and C. When the action ceases, a current of dry air is forced through C, to drive all the volatile product from the apparatus; the cap is then replaced, and the whole placed on the balance to be weighed. The loss of weight represents the volatile product.

The following results show the accuracy which may be expected when carbonates are treated in the apparatus with dilute hydrochloric acid:—

TABLE I.

Taken. Grm.	Found. Grm.	Error. Grm.
<i>Calcium Carbonate.</i>		
0.2000	0.0879	-0.0001
0.2000	0.0878	-0.0002
0.2000	0.0879	-0.0001
0.2000	0.0879	-0.0001
0.5000	0.2197	-0.0003
0.5000	0.2196	-0.0004
0.5000	0.2194	-0.0006
0.5000	0.2198	-0.0002
0.5000	0.2197	-0.0003
0.5000	0.2197	-0.0003
<i>Barium Carbonate.</i>		
0.5000	0.1134	-0.0011
0.5000	0.1137	-0.0005
0.5000	0.1137	-0.0005
0.5000	0.1136	-0.0006
<i>Strontium Carbonate.</i>		
0.5000	0.1485	-0.0004
0.5000	0.1486	-0.0003
0.5000	0.1485	-0.0004

TABLE II.

Taken. Grm.	Found. Grm.	Error. Grm.
<i>Magnesium Metal.</i>		
0.1000	0.0087	+0.0003
0.1000	0.0085	+0.0001
0.1000	0.0084	0.0000
0.1000	0.0084	0.0000
0.1000	0.0083	-0.0001
<i>Zinc Metal.</i>		
0.2000	0.0061	0.0000
0.2000	0.0062	+0.0001
0.2000	0.0062	+0.0001
0.2000	0.0060	-0.0001
0.2000	0.0061	0.0000

TABLE III.

Taken. Grm.	Found. Grm.	Error. Grm.
<i>Urea.</i>		
0.1000	0.0469	+0.0003
0.1000	0.0467	+0.0001
0.1000	0.0467	+0.0001
0.1000	0.0468	+0.0002
0.1000	0.0467	+0.0001
<i>Ammonium Oxalate.</i>		
0.1000	0.0204	+0.0007
0.1000	0.0197	0.0000
0.1000	0.0198	+0.0001
0.1000	0.0198	+0.0001
0.1000	0.0196	-0.0001
<i>Ammonium Chloride.</i>		
0.1000	0.0264	+0.0002
0.1000	0.0265	+0.0003
0.1000	0.0261	-0.0000
0.1000	0.0263	+0.0001
0.1000	0.0261	-0.0001

In Table II. are included the results of some experiments made to determine the weights of hydrogen liberated by the action of magnesium and zinc, upon dilute hydrochloric acid.

Determinations of the nitrogen liberated from urea, ammonium oxalate, and ammonium chloride, by action of sodium hypobromite, are given in Table III.

I wish to thank Prof. F. A. Gooch for his advice and kind assistance.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 18th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

Of the following papers, those marked * were read:—

*1. "*The Refractive Indices of Crystallising Solutions, with especial reference to the Passage from the Metastable to the Labile Condition.*" By HENRY ALEXANDER MIERS and FLORENCE ISAAC.

The authors found that the refractive index of a strong solution of sodium nitrate, measured at intervals while the liquid cools, rises to a maximum value and then falls, crystals appearing before the maximum is reached. If the solution is stirred during the process, the fall is very rapid, and is accompanied by a profuse shower of crystals. Other solutions (for example, alum, sodium chlorate, sodium thiosulphate, ammonium oxalate) behave in the same way. There are always two periods of crystallisation: a first, in which a few crystals are growing gradually; a second, in which many crystals appear spontaneously; so that in the latter the increase of index due to cooling is more than compensated by the decrease due to weakening of the solution. The authors regard these as being undoubtedly the metastable and labile states. This view is confirmed by the behaviour of the same solutions enclosed in sealed tubes, and shaken continuously; if the salt is completely dissolved, they cannot be made to crystallise until they have assumed a temperature corresponding to the maximum refractive index. By means of auxiliary experiments, the refractive indices are interpreted as concentrations, and each series of observations is expressed as a curve with concentrations for ordinates and indices for abscissae; the maximum points of the curve lie on a new curve, the "supersolubility curve" denoting the limit between the metastable and labile conditions; the same curve is given by the temperatures at which different solutions yield crystals when shaken in sealed tubes; it shows the highest temperature at which any given supersaturated solution can crystallise spontaneously. It is necessary in the case of sodium chlorate to employ friction as well as motion, by enclosing some insoluble substance in the tube, in order to make the crystals appear as soon as the supersolubility curve is reached.

In the experiments in open vessels, the refractive index is measured by means of a totally reflecting glass prism immersed in the liquid; the crystals which appear before the labile state is reached are doubtless introduced with the dust of the air, or are due to evaporation and cooling at the edges and surface of the liquid, which reduces the solution locally to the labile state.

DISCUSSION.

Dr. TUTTON said that it appeared to him that these interesting experiments lead to two important results. Firstly, that determinations of the refractive index of highly concentrated solutions afford valuable indications of the limits of the so-called "labile" and "metastable" conditions, and a new means of exploring the region of supersaturation. Secondly, that this new method of research may be of value in cases of dimorphism, where one of the

forms only is commonly obtained, by throwing some light on the reasons for the predisposition to crystallise in that particular form rather than in the other.

Sir WILLIAM RAMSAY asked whether Professor Miers had made any experiments on the condition of water cooled to below 4° from a high temperature, and produced from melted ice, but not allowed to rise above 4° . Experiments made by Mr. Wilsmore in his laboratory had failed to show any difference in density of different specimens of water thus prepared; but he understood that Dr. Chichester Bell had been successful in detecting different values for γ , the ratio of the specific heats at constant volume and constant pressure, in two such specimens of water; γ was determined by an acoustical method.

Mr. PICKERING said that the authors should be congratulated on having obtained a method of studying solutions at that critical period of their existence when crystallisation is occurring, and he suggested that it might be of advantage to study pure liquids in the same way.

In reply to a question from Prof. ARMSTRONG, Prof. MIERS said that the experiments reveal a state of the solution in which a sudden access of spontaneous crystallisation occurs, and this condition is indicated by the term "labile." He hoped to extend the experiments to water and other pure substances.

*2. "The Effect of Constitution on the Rotatory Power of Optically Active Nitrogen Compounds." (Part I.). By MARY BEATRICE THOMAS and HUMPHREY OWEN JONES.

The resolution of a set of optically active nitrogen compounds and the examination of the rotatory power of their salts in dilute aqueous solution have been made in order to find the rotatory power of the ions. This property of the ions is free from many of the disturbing influences such as molecular association and nature of solvent, which affect the rotatory power of non-electrolytes, and render comparable results so difficult to obtain with this class of compound.

Relations between rotatory power and constitution ought therefore to become more evident in the case of ions than of complete molecules.

Two homologous series, each consisting of five compounds, were chosen for examination; in one series, three of the hydrogen atoms in the ammonium ion are replaced by the phenyl, methyl, and allyl groups, whilst the fourth atom of hydrogen is replaced successively by the ethyl, *n*-propyl, *isopropyl*, *isobutyl*, and *isoamyl* groups; in the other series, the phenyl, methyl, and benzyl groups are present with the same five aliphatic groups. The ethyl compound of the latter series has already been described by one of us, and Wedekind has resolved the *n*-propyl and *isobutyl* compounds. The compounds originally resolved by Pope and Peachey, namely, the phenylbenzylmethylallylammonium salts, fall naturally into both these series.

The following are the values of $[M]_D$ for the ions at 15° :—

Phenylmethylallyl series. Ethyl, 16° ; *n*-propyl, 106° ; *isopropyl*, 103° ; *isobutyl*, 55° ; *isoamyl*, 18° ; benzyl, 167° .

Phenylmethylbenzyl series. Ethyl, 19.4° ; *n*-propyl, 299° ; *isopropyl*, 398° ; *isobutyl*, 323° ; *isoamyl*, 287° .

In all cases examined, the value of $[M]_D$ for the basic ion is diminished slightly with increasing temperature between 10° and 50° .

In both series there is a well-marked maximum of rotatory power at the second member of the series, the propyl or *isopropyl* compound; in the allyl series, the rotatory power of these two compounds is almost identical, but in the benzyl series the propyl compound occupies quite a different position.

The application of Guye's hypothesis to the case of nitrogen gives an expression for the rotatory power of the compound in terms of the masses of the substituting groups which does not account for the results in an entirely satisfactory manner.

In those cases where the active iodide could be recovered its rotatory power was examined in solution in alcohol and in chloroform.

The rotatory power was always greater in chloroform than in alcohol, and the iodides invariably underwent racemisation in chloroform solution with very different velocities.

*3. "The Determination of Available Plant Food in Soil by the Use of Weak Acid Solvents." By ARTHUR DANIEL HALL and ARTHUR AMOS.

The authors have investigated the effect of repeating the attack of weak acid solvents on soils of known history derived from the Rothamsted experimental plots. After the first extraction, the soil is washed, and again extracted with the same solvent, the process being repeated several times. The solvents employed were water charged with carbon dioxide and a 1 per cent solution of citric acid.

The first extraction does not remove the whole of the phosphoric acid capable of going into solution in the given solvent, the reaction is a reversible one, and a position of equilibrium is attained between the phosphoric acid in solution and the bases in the soil.

With carbon dioxide and water, the position of equilibrium is approximately constant for successive extractions and is characteristic of the manurial history of the soil. With dilute citric acid, the phosphoric acid going into solution falls for the first four or five extractions, and then becomes approximately constant. In the case of the Rothamsted soils, which have been continuously manured with superphosphate, the phosphoric acid going into solution decreases logarithmically, indicating that the amount dissolved is proportional to the active mass of a particular compound present in the soil, six-tenths of which become dissolved at each extraction. The total quantity of this compound is equal to the phosphoric acid supplied as manure during the last fifty years, less that which has been removed in the crop.

Soils which have received more varied compounds of phosphoric acid as manure do not show the same regular decrement in the amounts passing into solution, indicating the presence in the soil of a number of compounds of phosphoric acid of differing solubility.

The investigation lends no support to the theory that all soils establish in the soil water a solution of phosphoric acid of approximately the same composition and independent of the fertilisers the soil receives.

DISCUSSION.

Dr. DYER said the paper was one of much interest; for whilst in his original examination of these soils he had, by one extraction only with citric acid, found in the surface soil the greater part of the calculated accumulation of phosphoric acid due to the manuring, the authors had now, by their supplementary extractions with the same reagent, discovered the remainder almost with the accuracy of an accountant's balance sheet—except in the case of the dunged plots. In three cases, the earlier investigation showed that some of the phosphoric acid had gone down into the lower depths of the sub-soil, and, furthermore, the actual quantity of phosphoric acid added in the dung could only be vaguely guessed. It was satisfactory to hear that the authors still considered that for practical analytical purposes one extraction sufficed.

Mr. PICKERING asked whether the influence of the volume of solution used—which would mean a variation in the proportions of citric acid to soil—had been investigated, also whether the effect of pulverisation of the soil had been examined, for he had found that the amount of potash and iron dissolved by citric acid from a soil depended largely on the degree of fineness to which the soil had been reduced.

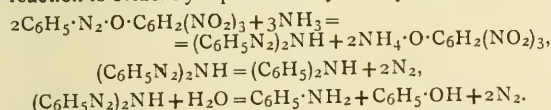
In reply, Mr. HALL said that in all cases the amount of citric acid solution had been kept constant, 1 litre to 100 grms. of the soil. Soil which passed the 3 m.m. sieve was used without any grinding, but as there were other reasons for supposing that the soil phosphates were almost wholly found on the outside of the soil particles, grinding should not make much difference to the phosphoric acid results.

*4. "The Action of Ammonia and Amines on Diazobenzene Picrate." By OSWALD SILBERRAD and GODFREY ROTTER.

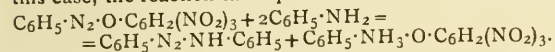
When diazobenzene picrate is acted on by ammonia gas, it rapidly loses the characteristics of a diazo-salt, and forms a dark red product.

Two possibilities presented themselves, namely:—(1) The formation of ammonium picrate, accompanied by further reactions between the diazo-complex and the excess of ammonia; (2) an intramolecular transformation of the diazo-picrate to trinitrobenzeneazophenol, somewhat analogous to the diazoaminobenzene transformation.

The intense red colour of the product appeared to lend some probability to the latter assumption, but an examination of the reaction completely disproved the presence of azo-compounds. The products proved to consist mainly of ammonium picrate, and diphenylamine, aniline, and phenol were also detected. Thus, the course of the reaction is evidently represented by the equations—



Other compounds occurred in small quantities as the result of secondary reactions. When treated with aniline, diazobenzene picrate gives rise to aniline picrate and aminoazobenzene; the latter compound evidently resulted from a transformation of diazoaminobenzene; thus, in this case, the reaction takes place as follows:—



DISCUSSION.

Dr. MORGAN stated that in conjunction with Mr. Wootton he had studied the picrates of diazo-compounds, and especially the stable product derived from *p*-aminobenzanilide (*Proc.*, xxii., p. 23). This compound was precipitated even in strongly acid solution, and was therefore in all probability a diazonium derivative. They had not detected *syn*- and *anti*-isomerism in this series. It would be interesting to know whether the more explosive diazobenzene picrate was a diazo-compound or a diazonium salt.

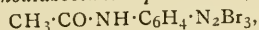
In reply, Dr. SILBERRAD said that the comparative stability of diazobenzene picrate was remarkable considering its constitution, but, nevertheless, he regarded it as a true diazonium salt. Under these conditions, it seemed improbable that *syn*- and *anti*-derivatives could be prepared, which was in accord with Dr. Morgan's observations on similar compounds.

*5. "The Preparation of Bistriazobenzene." By OSWALD SILBERRAD and BERTRAM JAMES SMART.

The explosive properties of bistriazobenzene have hitherto precluded the verification of its composition by analysis; for this reason, a re-investigation of the compound has been undertaken, and at the same time the method for its preparation has been somewhat modified.

Griess (*Ber.*, 1888, xxi., 1559) took the oxamic acid of *p*-phenylenediamine as the starting-point for the preparation of this compound; in the present work, however, it has been found advantageous to proceed from *p*-aminoacetanilide. The successive steps of the preparation are seen from the following series of intermediate products:—*p*-Aminoacetanilide, acetyl-*p*-aminodiazobenzene perbromide, *p*-aminotriazobenzene, *p*-triazodiazobenzene perbromide, bistriazobenzene.

Acetyl-*p*-aminodiazobenzene perbromide,—



crystallises in small yellow plates (m. p. 126°) with decomposition.

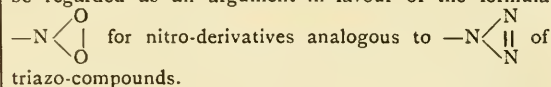
p-Aminotriazobenzene, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_3$, was prepared by the hydrolysis of acetyl-*p*-aminotriazobenzene with caustic potash, previously unsuccessfully attempted by Rupe and von Majewski (*Ber.*, 1900, xxxiii., 3406).

Bistriazobenzene, $\text{N}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}_3$ (m. p. 83°) explodes on heating; its analysis was, however, successfully carried out under diminished pressure, and gave results which agreed with the above formula.

DISCUSSION.

Dr. FORSTER inquired whether *p*-bistriazobenzene has a distinctive odour, because he had noticed that *m*- and *p*-nitrophenylazoimides have a faint odour of anise, which is more marked in the case of *p*-tolylazoimide and *p*-chlorophenylazoimide, whilst in the case of *p*-methoxyphenylazoimide the odour is comparable with that of anethole itself, being less sweet and more pungent than the perfume of the last-named substance. Curiously enough, *o*-nitrophenylazoimide is odourless.

In reply, Dr. SILBERRAD said that he had noticed an anise-like odour, but considered the smell more similar to that of a nitro-compound, and suggested that this might be regarded as an argument in favour of the formula



*6. "Gradual Decomposition of Ethyl Diazoacetate." By OSWALD SILBERRAD and CHARLES SMART ROY.

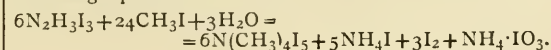
When ethyl diazoacetate is exposed to light at the ordinary temperature, a gradual evolution of nitrogen occurs, and after the space of several years, thick colourless rhombic crystals resembling cane-sugar gradually make their appearance. On examination, this compound proved to be the triethyl ester of 4:5-dihydro-3:4:5-pyrazoletricarboxylic acid.

Subsequent work showed that the same compound can readily be produced by warming ethyl diazoacetate with copper dust. In both cases, the reaction is evidently due to the intermediate formation of fumaric or maleic esters.

This view is confirmed by the work of Buchner and Witter, who prepared the trimethyl ester by the action of the corresponding ester of fumaric or maleic acid on methyl diazoacetate (*Annalen*, 1895, cclxxiii., 239).

*7. "Studies on Nitrogen Iodide. III. The Action of Methyl and Benzyl Iodides." By OSWALD SILBERRAD and BERTRAM JAMES SMART.

The Action of Methyl Iodide.—Previous experiments by Stahlschmidt (*Poggendorff's Ann.*, 1863, cxix., 421) on the interaction of nitrogen iodide with methyl iodide led him to represent the reaction by the following equation:— $2\text{NI}_3 + 6\text{CH}_3\text{I} = \text{N}(\text{CH}_3)_4\text{I}_5 + \text{NH}_4\text{I} + 2\text{CHI}_3$. Since the formula here assumed for nitrogen iodide is not in accord with that proved by Chattaway (*Proc.*, 1899, xvii., 20; *Am. Chem. Soc.*, 1900, xxiii., 363, &c.), or with the constitution $\text{NI}_3:\text{NH}_3$, established by one of the authors (Silberrad, *Trans.*, 1905, lxxvi., 55 and 66), renewed experiments have been carried out on the above reaction. The formation of tetramethylammonium pentaiodide as observed by Stahlschmidt was confirmed in the present work, and its nature established by its preparation from tetramethylammonium iodide and iodine. Iodoform was not, however, as he believed, a product of the reaction between nitrogen iodide and methyl iodide, but resulted from the alcohol present in his experiments. In the present work, alcohol was excluded; the nitrogen iodide was prepared from ammonia and iodine chlorine, and was allowed to react with excess of methyl iodide under water. The products found were tetramethylammonium pentaiodide, ammonium iodide and iodate, and free iodine. The quantities of all these products were determined, and the reaction was proved to proceed almost quantitatively according to the following equation:—



No compounds corresponding to Stahlschmidt's di-iodomethylamine or butyric acid were produced.

Action of Benzyl Iodide.—This iodide was found to react readily with moist nitrogen iodide. The nature of

products, however, depends on the proportion of benzyl iodide taken, bright green or garnet-red crystals being deposited according to the conditions of the experiment. These proved both to be periodides of tribenzylamine.

Tribenzylammonium Pentaiodide, $N(C_6H_5)_3HI_5$, which forms bright green crystals melting at $121-122^\circ$, is sparingly soluble in alcohol, and undergoes a slight decomposition on re-crystallisation.

Tribenzylammonium Di-iodide, $N(C_6H_5)_3HI_2$, crystallises in garnet-red prisms melting at $115-116^\circ$; it dissolves more readily in alcohol than the pentaiodide, and can be more easily obtained in the crystalline condition.

The pentaiodide can be readily converted to the red di-iodide by the partial abstraction of its iodine by shaking with potassium iodide solution. Conversely, the di-iodide can be converted into pentaiodide by treatment with alcoholic iodine. Both compounds can also be obtained direct from tribenzylamine by the addition of the required quantity of iodine to the iodide of the base.

*8. "Action of Bromine on Benzeneazo-o-nitrophenol." By JOHN THEODORE HEWITT and NORMAN WALKER.

By the action of bromine on 4-benzeneazo-2-nitrophenol in presence of glacial acetic acid and fused sodium acetate, the 6-hydrogen atom is replaced. The constitution of the resulting compound, which when pure melts at $154.5-155^\circ$, was confirmed by fission with excess of fuming nitric acid. The resulting *p*-nitrophenyldiazonium nitrate was isolated by conversion into *p*-nitrobenzeneazo-*B*-naphthol, whilst 1.5 grms. of 2-bromo-4:6-dinitrophenol, melting before purification at 116° (uncorr.), were obtained instead of the theoretical amount of 1.6 grms. from 2 grms. of the azophenol. Körner gives the melting-point of bromodinitrophenol at 118° .

The following derivatives of benzeneazobromonitrophenol have been analysed:—Sodium and potassium salts, acetyl derivative (m. p. 137°), and benzoyl derivative (m. p. 131°). 4-*p*-Toluenazo-2-nitro-6-bromophenol was prepared in a similar manner from *p*-toluenazonitrophenol; it melts at 161° . Fuming nitric acid furnishes 2-bromo-4:6-dinitrophenol as a product of fission; its acetyl derivative melts at 124° , the benzoyl derivative at 129° .

*9. "The Condensation of Dimethyldihydroresorcin and of Chloroketodimethyltetrahydrobenzene with Primary Amines. Part I. Monoamines, Ammonia, Aniline, and *p*-Toluidine." By PAUL HAAS.

Dimethyldihydroresorcin reacts with ketonic reagents as a diketone; in most of its other reactions, however, it behaves as a hydroxyketone having the formula $CM_2 < \begin{smallmatrix} CH_2 \cdot C(OH) \\ CH_2 \cdot CO \end{smallmatrix} = CH$. In this form, it condenses

with a single molecule of a primary amine by the elimination of water between the hydroxyl group and the amino-hydrogen, giving rise to a secondary amine. This replacement of the hydroxyl group by a basic group $-NHR$ caused the remaining ketonic oxygen to become hydroxylic, as shown by the fact that the new substance gives a colour reaction with ferric chloride and does not react with ketonic reagents; when, however, the basic substituting group is rendered more acid by acetylation, the resulting compound no longer gives any coloration with ferric chloride, and condenses with semicarbazide, showing that the oxygen atom has become ketonic.

Chloroketodimethyltetrahydrobenzene, unlike dimethyldihydroresorcin, reacts at once with two molecules of a primary amine, giving rise to the hydrochloride of a mixed secondary and tertiary base having the formula $CM_2 < \begin{smallmatrix} CH_2 \cdot C(NHR) \\ CH_2 \cdot C(NR) \end{smallmatrix} = CH$. Bases of this type may also be prepared by condensing the mono-substituted derivatives, obtained by the action of dimethyldihydroresorcin on the amine, with a second molecule of the same amine in the presence of zinc chloride.

10. "Silicon Researches. Part X. Silicon Thiocyanate." By J. EMERSON REYNOLDS.

The author found that silicon thiocyanate, $Si(SCN)_4$, is

best prepared by prolonged digestion of pure lead thiocyanate in a benzene solution of silicon tetrachloride. An excess of the lead salt must be used, as the latter exchanges but one of its two thiocyanogen groups for chlorine, forming the yellow crystalline compound $PbCl(SCN)$, silicon thiocyanate remaining in solution. The latter compound is obtained in fine white crystals, when most of the benzene is removed by distillation; but if any moisture is present the crystals become yellow owing to decomposition. This method of preparing the thiocyanate gives a much better product than Miquel's (*Ann. Chim., Phys.*, 1877, [v.], xi., 343), in which the materials are heated to about 400° , as in this investigator's process charring results, and an impure substance is obtained.

The pure thiocyanate melts at 143.8° (corr.) and boils at 314.2° (corr.), distilling without decomposition.

The chief interest attaches to the constitution of the compound, as the somewhat analogous phosphorus "trithiocyanate" has been shown by A. E. Dixon (*Trans.*, 1901, lxxix., 541) to exhibit "a form of tautomerism," in some cases acting as $P(NCS)_3$, and in others as $P(SCN)_3$.

The author has compared silicon thiocyanate with the phenylamide, $Si(NH \cdot C_6H_5)_4$, described in Part V. of this series of papers, and has examined several interactions of the thiocyanate with aniline and other substances, and concludes from the results that it is correctly represented by the expression $Si(SCN)_4$.

11. "Halogen Derivatives of Substituted Oxamides." By FREDERICK DANIEL CHATTAWAY and WILLIAM HENRY LEWIS.

The action of the halogens on substituted oxamides has been little studied, and the description given of the substances formed is not very satisfactory, as the crude products obtained were not subjected to any process of purification. The action of chlorine on oxanilide has been studied, and a number of substituted oxanilides has been prepared in a simpler way in order to compare them with the foregoing products.

The usual product of the chlorination of oxanilide is a mixture of *s*-di-*p*-chlorophenyloxamide and of its *s*-dichloro-amino-derivative.

When aniline or a substituted aniline is heated with ethyl oxalate, a symmetrical disubstituted oxamide on the ethyl ester of a substituted oxamic acid is formed according as the aniline or the ethyl oxalate is in excess.

The symmetrical chlorophenyloxamides, which are almost insoluble in ordinary solvents, crystallise well from nitrobenzene, in which on heating they readily dissolve.

The following compounds were described:—*s*-Di-*p*-chlorophenyloxodichloroamide, colourless rhombs (m. p. 169°); ethyl *p*-chlorophenyloxamate, colourless plates (m. p. 155°); *p*-chlorophenyloxamide, colourless needles (m. p. 241°); *s*-di-*p*-chlorophenyloxamide, colourless thin plates (m. p. 288°); ethyl 2:4-dichlorophenyloxamate, colourless, hair-like prisms (m. p. 119°); 2:4-dichlorophenyloxamide, colourless, hair-like crystals (m. p. 234°); *s*-di-2:4-dichlorophenyloxamide, colourless, slender prisms (m. p. 276°); *s*-dimethyloxodichloroamide, colourless, slender prisms (m. p. 37°); *s*-diethyloxodichloroamide, pale yellow, viscid liquid which decomposes on heating; *s*-dimethyloxodibromoamide, pale yellow, flattened prisms (m. p. 95°); *s*-diethyloxodibromoamide, pale yellow plates (m. p. 82°).

12. "Menthyl Benzenesulphonate and Menthyl Naphthalene-6-sulphonate." By THOMAS STEWART PATTERSON and JOHN FREW.

Menthyl benzenesulphonate and menthyl naphthylene-6-sulphonate have been prepared by the pyridine method. The former crystallises from alcohol in silky needles melting at 80° , the latter separates from alcohol in solid, opaque crystals melting at $114-114.5^\circ$. The compounds themselves decompose on continued heating at or above the melting-point, so that their rotations have been determined in high alcohol, benzene, and nitrobenzene. The chief points of interest are as follows.—1. There is con-

siderable variation of rotation with change of solvent. 2. The values of $[M]_D$ for the β -naphthalene compound are consistently lower than for the benzenesulphonate in a given solvent. 3. The solvents, however, do not exert proportionate influences on the rotations of the two compounds. 4. Menthyl benzenesulphonate has a lower molecular rotation than menthyl benzoate by about 56° , and menthyl naphthalene- β -sulphonate a lower rotation than menthyl β -naphthoate by about 113° . 5. As regards the influence of temperature change on the rotations of these compounds in solution, it was found that the greater the rotation produced by a solvent the more rapid was its diminution with rise of temperature. The molecular rotations in dilute solution seem to tend at higher temperatures towards a common value of about -170° .

13. "Some Reactions and New Compounds of Fluorine." By EDMUND BRYDGES RUDHALL PRIDEAUX.

The fluorine was prepared by the electrolysis of anhydrous hydrogen fluoride contained in a copper vessel (Moissan, "Le Fluor et ses Composés"). In every case when the gas was analysed it was found to contain oxygen, and special experiments proved that this oxygen was produced at the anode even after the current had passed for a considerable time.

Liquid fluorine has no solvent or chemical action on iodine. The colourless iodine fluoride was analysed by a volumetric method, and four concordant percentages of iodine confirmed the formula IF_5 established by Moissan (Comptes Rendus, 1902, cxxxv., 563) from the results of gravimetric analysis.

Bromine fluoride was prepared for the first time; analyses carried out by a gravimetric method led to the formula BrF_3 . Liquid fluorine has neither solvent nor chemical action on solid bromine.

Gaseous fluorides of selenium and tellurium were prepared by the direct combination of the elements in the cold. The formulae of these gases were proved to be SeF_6 and TeF_6 by determinations of their densities. Analysis of TeF_6 also showed it to have this formula. These gases are colourless and easily condensable by moderate cold or pressure to white crystalline solids and colourless liquids respectively. Tellurium hexafluoride has an unpleasant odour, and decomposes water slowly at 15° ; selenium hexafluoride does not decompose water at 15° .

The vapour pressure curve of SF_6 was determined for comparison with those of SeF_6 and TeF_6 . The three curves resemble one another closely. In the case of SF_6 and SeF_6 , the melting-points lie above the temperatures at which the vapour over the solid attains a pressure of 760 m.m., whilst in the case of TeF_6 the melting-point lies just below the boiling-point. The critical temperatures of the liquefied gases rise in the order SF_6 , SeF_6 , TeF_6 .

The molecular volumes at temperatures equally removed from the melting-points were found to be very nearly the same.

The refractivities of the three compound gases bear no simple additive relation to those of their constituent elements.

The refractivities minus a constant are directly proportional to the densities of the gases.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, January 26th, 1906.

Prof. J. H. POYNTING, F.R.S., President, in the Chair.

A PAPER on "The Isothermal Distillation of Nitrogen and Oxygen and of Argon and Oxygen" was read by Mr. I. K. INGLIS.

Mixtures of liquid nitrogen and oxygen are particularly suitable for an exact study of the relations obtaining during isothermal distillation; for the distillation bulb being the coldest instead of the hottest part of the apparatus, errors

due to back condensation, &c., can be eliminated. In addition the vapour can easily be circulated and passed time after time through the liquid until equilibrium is complete. Experiments were carried out in this way in a specially designed apparatus, and the results showed that the ratio of nitrogen to oxygen in the vapour was not in a constant proportion to the same ratio in the liquid. When, however, the partial pressures of nitrogen and oxygen were plotted against the concentrations in the liquid, a straight line was obtained in the case of nitrogen and a curve in the case of oxygen. This indicated that nitrogen obeyed Henry's law of solubility, and the deviation in the case of oxygen pointed to its being slightly associated in the liquid state when mixed with nitrogen. A few experiments were also carried out with mixtures of argon and oxygen. At the temperature used argon was a volatile solid, and therefore the greatest concentration of argon that could be obtained was that of the saturated solution in oxygen. Argon seemed to agree with nitrogen in obeying Henry's law.

Dr. J. A. HARKER said the paper was interesting at the present time, as in the *Journal de Physique* for January a new process for obtaining liquid oxygen commercially and with the expenditure of a little power was described, in which advantage was taken of the difference in composition of the liquid and the vapour in the distillation of liquid air.

A paper on "The Use of Chilled Cast-iron for Permanent Magnets" was read by Mr. A. CAMPBELL.

The experiments described were undertaken with a view to corroborating and extending the results already obtained by other experimenters. A good many years ago Mr. J. R. Ashworth showed that rods of chilled cast-iron could be made into very fair permanent magnets; and last year Mr. B. O. Peirce, of Harvard University, published an interesting research on the subject, going considerably farther, and describing the practical utility of chilled cast-iron for magnets of moving-coil galvanometers and other instruments. His tests, although conclusive in many ways, did not in general give any absolute values (for permeability, &c.). The present investigation was made on rings in addition to rods of the standard dimensions usual in testing magnet-steels. All the specimens were heated to $1000^\circ C.$, and then chilled in cold water, care being taken to support them during the process, as cast-iron is very brittle at such a high temperature. The rods were tested for maximum remanent B and coercivity by Madame Curie's method, the magnetised bar being placed in a long solenoid producing a demagnetising field which was gradually increased until a search-coil slipped along the bar showed that the demagnetisation was complete. The results showed the chilled cast-iron to be not very inferior to ordinary magnet steel. By ballistic tests on the two rings, their permeability curves were obtained, and these indicated that the simple process of chilling used was quite satisfactory even for a tolerably massive ring of 6 sq. c.m. cross section. The cheapness and ease of working cast-iron should encourage instrument-makers to test its capabilities in various instruments.

Mr. W. H. PRETTY asked the author what kind of cast-iron he had used in his experiments. The physical properties of cast-iron varied with the chemical composition, and it was important that the kind of iron used in the experiments should be stated.

The AUTHOR, in reply to Mr. Pretty, said the iron used was grey commercial cast-iron, but Mr. Ashworth had tested several kinds and found very little difference in their magnetic properties.

A paper by Prof. LYLE and Mr. BALDWIN, "On Experiments on the Propagation of Longitudinal Waves of Magnetic Flux along Iron Wires and Rods," was read by Prof. F. T. TROUTON.

The experiments described in the paper were undertaken with the object of determining if there is a definite rate of propagation of magnetism in iron. The method adopted

was to produce magnetisation at a particular point on a bar by means of a coil through which an alternating current was passed, and then to observe the magnetic flux at various distances from the coil by means of a small secondary coil, free to be moved to various places on the bar. By the use of Prof. Lyle's wave-tracer the magnetic flux at various points along the bar was thus obtainable. The wave curl was then analysed by Fourier's series. Various curves given in the paper show the value of the constants in Fourier's series, and of the lag in the magnetisation as the coil was moved along the bar. Contrary to what had been observed in previous researches, the authors found that the phase lag, instead of continuously increasing along the bar, reached a maximum value and then diminished, proving the absence of true wave propagation.

Prof. TROUTON read a letter from Mr. A. W. PORTER pointing out that the occurrence of a maximum in the phase lag was exactly what was to be expected on any theory which made the lag depend upon a direct power of both permeability and distance.

CORRESPONDENCE

THE TEMPERATURE OF SOLUTIONS HEATED BY OPEN STEAM.

To the Editor of the Chemical News.

SIR,—Allow me to correct the erroneous impression—conveyed by Mr. Steel's article on the above subject (CHEMICAL NEWS, vol. xciii., p. 42)—that, although Peter Spence discovered that open steam would heat solutions to higher temperatures than its own, and described his experiments in detail in the *Brit. Assoc. Trans.* for 1869, he had no explanation to give of the phenomenon; and that the first person to theoretically account for it was H. Claassen, thirty-five years after (*i.e.*, in 1904).

The simple fact is: the explanation has been familiar at these works and elsewhere ever since 1869.

I append in evidence of this the subjoined extract from p. 31 of the *Brit. Mer. Gazette* for July, 1878.—I am, &c.,

FRANK SPENCE, Chairman,
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"Some very important scientific discoveries have been made by Mr. Spence, apart from those more directly affecting his own branch of the chemical industry, whilst prosecuting his experiments and studies. He ascertained that steam of 212° F. could be made to raise the temperature of saline solutions to their boiling-point, however high that boiling-point might be. Thus a solution of acetate of potash might be readily raised by open steam to a temperature of 336° F. This result appeared so paradoxical that on Mr. Spence reading a paper on the subject, at the Exeter Meeting of the British Association, his statements were received with incredulity until the actual experiment was successfully made before his auditory, which included Prof. Williamson and other able chemists. The fact being proved, the explanation, as in the case of Columbus and the egg, was readily received, *viz.*, that the latent heat evolved by the condensing steam became sensible heat, measurable by the thermometer."

COLOUR AND STRUCTURE.

To the Editor of the Chemical News.

SIR,—The relation between constitution and physical properties has been a matter of the deepest interest to chemists for many years, but your readers may not be

aware that it is beginning to attract the sympathetic attention of the British working man.

At this end of the General Election everybody must be familiar with the illustrated Anti-Tea Duty poster, entitled "It Don't seem Right to Me." On my way to the meeting of the Chemical Society last Thursday, when there was some discussion on the above subject, a pamphlet was placed in my hands, also entitled "It Don't seem Right to Me." The pamphlet is in the following terms:—

"Talk of no colour without quinone;
Well, I'll tell you what I think:
There's many a compound isn't blue,
What's neither green nor pink.
No, neither pink nor green they are,
And it don't seem right to me,
To say that a compound ain't a quinone
When the N's double-linked with C."

I enclose my card, and subscribe myself,—Yours, &c.,

ETHENOID LINKAGE.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 2, January 8, 1906.

New Type of Compound in the Rare Earth Group of Metals.—C. Matignon and E. Cazes.—Anhydrous samarium chloride, SmCl_3 , has the property of being reduced by hydrogen, giving rise to a sub-chloride. This reduction necessitates a high temperature, and is best performed in a thick tube of Jena glass. The substance blackens when the reduction starts, and then melts and apparently boils, owing to the evolution of hydrochloric acid gas. The reaction is reversible, and can be expressed by the following equation:— $\text{SmCl}_3 + \frac{1}{2}\text{H}_2 \rightleftharpoons \text{SmCl}_2 + \text{HCl}$. The reduction can be better effected by using ammonia gas:— $3\text{SmCl}_3 + 4\text{NH}_3 = 3\text{SmCl}_2 + 3\text{NH}_4\text{Cl} + \text{N}$. It seems probable that praseodymium and neodymium are susceptible of also forming a sub-chloride under suitable conditions.

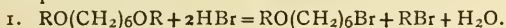
Electrolytic Preparation of Spongy Tin.—D. Tommasi.—The apparatus which may be used for the preparation of spongy tin consists of a rectangular vessel containing a solution consisting of 50 parts of water, 10 parts of stannous chloride, and 1 part of hydrochloric acid. Into this bath two tin anodes are placed, between which is a cathode consisting of a copper disc fixed by its centre in such a manner as to be capable of rotation, so that half the disc is always in contact with the air and half with the liquid.

Cuprous Silicide.—Em. Vigouroux.—The author confirms a set of experiments which he performed in 1901 on pure copper silicides, in which he finds the proportion of combined silicon very nearly 10 per cent. He also now isolates cuprous silicide, Cu_4Si , and examines its principal properties.

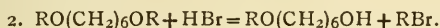
Reduction of Silver and Copper Chlorides by means of Calcium.—L. Hackspill.—By heating in a porcelain vacuum tube an iron boat containing variable proportions of silver chloride and calcium, the author obtains alloys in which the proportion of calcium can be as great as 45 per cent:— $2\text{AgCl} + n\text{Ca} = \text{CaCl}_2 + (n-1)\text{Ca} + 2\text{Ag}$. The above reaction takes place at a dull red heat. An examination of the silver and calcium alloys shows them to have a totally different appearance from silver; they are grey, crystalline, and can easily be powdered. When heated in the air they rapidly oxidise. After being heated for some time in air all the calcium is transformed into lime, which floats on the surface of the silver. All the alloys are attacked by cold water.

Asymmetric Derivatives of Hexanediol-1.6-diethyl Ether and Heptanediol-1.7-diiodide.—

R. Dionneau.—When hydrobromic acid acts on the ether oxides of hexanediol-1.6 in the cold, the following reaction takes place:—



This reaction is most complex. On the side of the non-transformed ether are bodies of alcoholic function, amongst which hexamethylene glycol has been isolated and recognised by its fusing-point. Besides Reaction 1, which produces the bromide function on the hexamethylene group, there is a secondary reaction which gives rise to the alcoholic function:—



Certain Derivatives of the Fatty Carbides produced by Hydrogenation by means of Ammonium Metals. Preparation of Ethylenic and Formenic Carbides.—E. Chablay.—The author finds that the molecule of an alkaline ammonium metal reacts as a hydrogenating agent on the bi-substituted halogen derivatives, and also on tri-substituted derivatives, with the condition that all substitutions must be made on the same atom of carbon. Such a molecule, on the contrary, reacts simply by virtue of its alkaline metal when the two substitutions are made on different carbons. The example of trimethylene bromide seems to indicate that the reactions have a specially simple character when the double substitution is made on two neighbouring atoms of carbon.

MISCELLANEOUS.

Royal Institution.—On Thursday next, February 15, at 5 o'clock, Mr. H. B. Irving delivers the first of two lectures at the Royal Institution on "The English Stage in the Eighteenth Century"; and on Saturday, February 17, at 3 o'clock, Mr. M. H. Spielmann begins a course of two lectures on "George Frederick Watts as a Portrait Painter." The Friday Evening Discourse on February 16 will be delivered by Mr. W. C. D. Whetham on "The Passage of Electricity through Liquids," and on February 23 by Professor J. O. Arnold on "The Internal Architecture of Metals."

Relative Vapour Tensions of the Three Different Modifications of Carbon.—A. Smits.—Rudolf Schenck and W. Heller (*Berichte*, 1905, xxxviii., 2139; *CHEMICAL NEWS*, 1905, xcii., 83) have shown that the different modifications of carbon possess different amounts of free energy, and that the equilibrium constants between CO , CO_2 , and the different forms of solid carbon must have different values at the same temperature, being greatest for the most labile form and least for the most stable. But the authors now point out that, though these statements are quite correct, the phenomena may be regarded in a different light, the difference in the values of the equilibrium constants being due to the different vapour tensions of the modifications of carbon at the same temperature. From the equilibrium equations it appears that the equilibrium pressures are proportional to the vapour tensions of the different varieties. If we imagine a closed exhausted space containing diamond and graphite, both forms would emit carbon vapour, the diamond more than graphite because its vapour tension is greater. It would then be expected that as soon as the vapour tension had exceeded that of graphite the carbon vapour would condense to graphite, which is not the case. Therefore we must assume that the carbon pressure rises to the vapour pressure of diamond. The vapour is supersaturated as regards graphite, and yet no condensation takes place. This phenomenon probably often occurs in the case of substances with very low vapour tensions. As regards the system consisting of ferrous oxide and one of the metastable forms of carbon, Schenck and Heller have shown that the carbon which is formed from carbon monoxide in contact with iron is graphite. Thus while carbon dioxide

is reduced by diamond carbon vapour to the monoxide, the latter yields graphite instead of diamond, and the metastable form disappears. The author has come to the conclusion that Schenck and Heller in their experiments with amorphous carbon and diamond did not measure the equilibrium pressures, and that if they had been able to continue their experiments they must have observed a decrease of the equilibrium pressure with amorphous carbon and diamond, until that pressure had been reached which corresponds to graphite. From their experiments it appears that although the absolute magnitude of the vapour tension of carbon is so small it is quite appreciable in equilibrium work of this kind.—*Berichte*, xxxviii., No. 17.

MEETINGS FOR THE WEEK.

- MONDAY, 12th.—Society of Arts, 8. (Cantor Lectures). "Modern Warships," by Sir William White, F.R.S., &c.
TUESDAY, 13th.—Royal Institution, 5. "Food and Nutrition," by Prof. William Stirling, M.D., &c.
WEDNESDAY, 14th.—Society of Arts, 8. "The Horseless Carriage, 1885—1905," by Claude Johnson.
THURSDAY, 15th.—Royal Institution, 5. "The English Stage in the Eighteenth Century," by H. B. Irving, M.A.
Society of Arts, 4.30. "The Navigable Waterways of India," by Robert B. Buckley, C.S.I.
Chemical, 8.30. "Cuprous Formate," by A. Angel.
"Solubility of Triphenylmethane in Organic Liquids with which it forms Crystalline Compounds," by H. Hartley and N. G. Thomas.
"Spontaneous Crystallisation of Supersaturated Solutions," by H. Hartley. "Preparation and Properties of some New Tropenes," by H. A. D. Jowett and A. C. O. Hann. "Studies in Asymmetric Synthesis—Part IV., The Application of Grignard's Reaction for Asymmetric Syntheses," by A. McKezie.
FRIDAY, 16th.—Royal Institution, 9. "The Passage of Electricity through Liquids," by W. C. D. Whetham, F.R.S.,
SATURDAY, 17th.—Royal Institution, 3. "George Frederick Watts, as a Portrait Painter," by M. H. Spielmann.

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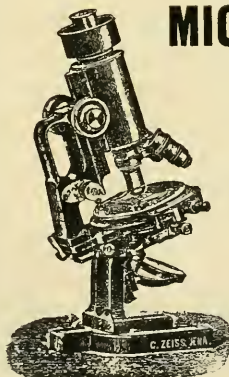
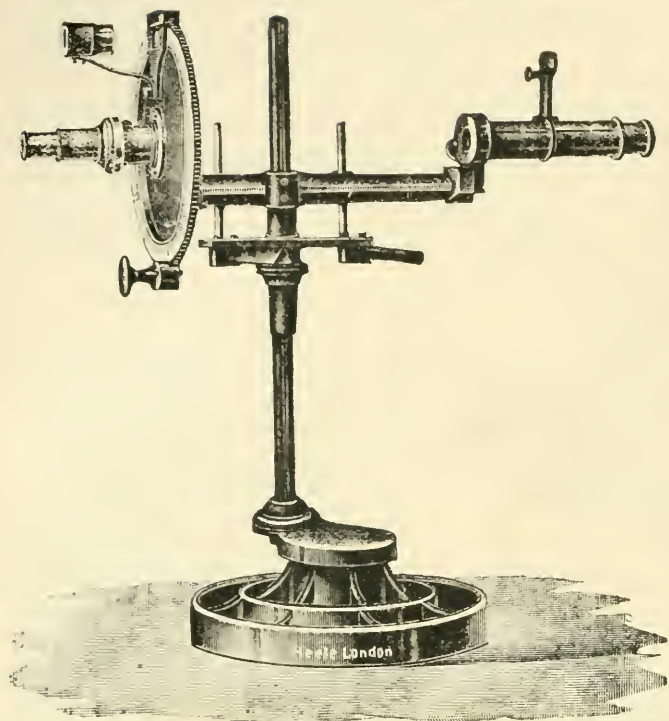


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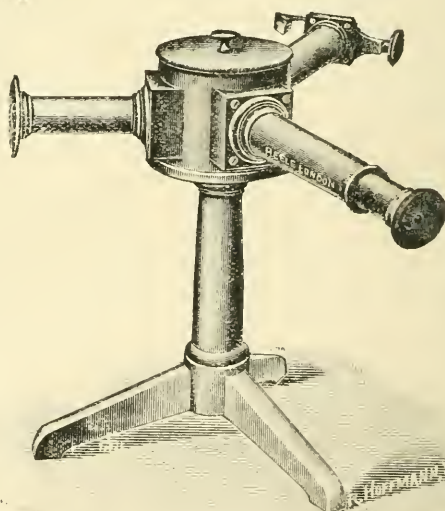
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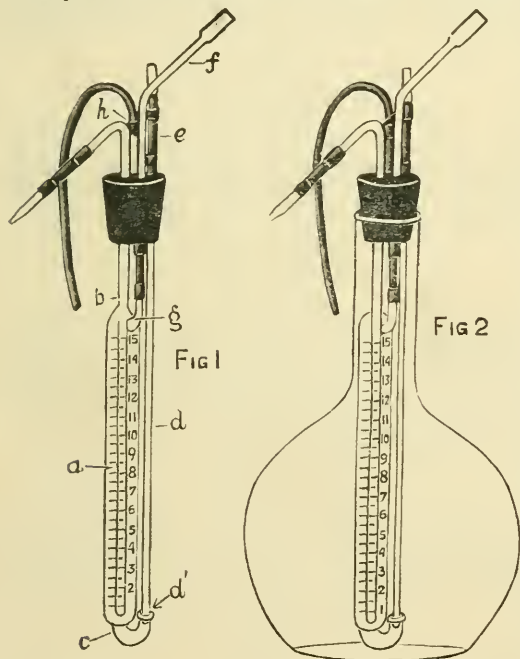
THE CHEMICAL NEWS.

VOL. XCIII., No. 2412.

NOTE ON A COMBINED WASH-BOTTLE AND PIPETTE.*

By J. W. HOGARTH.

DURING some chemical work in which it was desirable to dissolve a precipitate, with which the work was concerned, in a known volume of acid, the want was felt of a vessel possessing the combined advantages of a measuring vessel and wash-bottle. It was not originally intended to have devoted a separate article to the description of the apparatus which is described below, but because the work for the time being has been stopped, it was deemed advisable to now make mention of the vessel. Ordinarily when it is wished to dissolve or wash a precipitate with a known volume of solution, a measured quantity of the hot or cold liquid is poured into the filter containing the substance to be dissolved or washed, in which manner it is not possible to stir up the precipitate and thereby offer as large a surface as possible to the action of the solution, consequently



more liquid has to be used than is necessary to bring about the desired change; this excess of solution in some cases may be objectionable. If the liquid is delivered from a wash-bottle the objections to a great extent are obviated, but the volume of liquid used cannot conveniently be arrived at, especially when the filtrate has to be quantitatively treated, because any extra operation tends to introduce errors into the analysis. The apparatus of which the following is a description was designed to overcome the above objections.

The measurements given are those of the actual apparatus made for use. Vessel *a*, which is of thin glass 13.3 c.m. long, and 1.4 c.m. wide, is graduated in cubic centimetres

and fractions thereof. Tube *b* is 5 m.m. in diameter and 13.3 c.m. long from junction at top of *a* to the bottom where it just enters *c* (to bring *b* out more clearly for the purpose of photographing, it was partly filled with coloured liquid). Tube *g* is sealed on to *a*, and is connected to the lower extremity of *f* by a piece of stout rubber tubing. To use the vessel, rod *d* is slightly raised, the water-tight joint at *d'* where rod *d* is ground into *c*, is thereby broken, air is blown from the mouth through the rubber connected to *h*, which is in direct communication with the air of flask only, until the level of liquid rises to the desired mark in *a*; rod *d* is then released, when it is automatically forced back into position by the rubber *e*, which is stretched from the disc on *d* to the out-turned edge of a short glass tube through which *d* passes. This liquid is then delivered in the ordinary way by blowing into *f*; as soon as the liquid in *a* falls to the curved tube *c* liquid ceases to pass up *b*.

The vessel, which was of 15 c.c. capacity, delivered any desired volume within that limit to $\pm \frac{1}{2}$ c.c. Fig. 2 shows the apparatus as it fits in ordinary flask. As far as can be ascertained this apparatus has not elsewhere been described.

The author here takes the opportunity of tendering his thanks to Acting Professor Schofield for the interest shown and encouragement that he has often given him.

A BURETTE-FILLING DEVICE.

By EDWARD FRENCH.

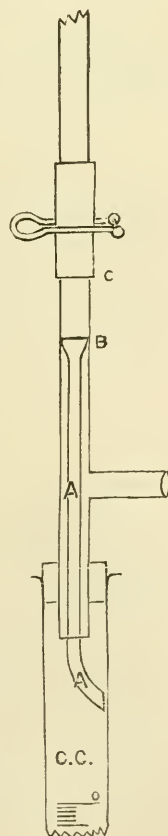
EVERY one who has worked with burettes having side tubes and stopcocks for filling the instrument appreciates the advantages gained by such a device over the old way of filling, by means of a funnel, from the bottle containing the standard solution.

In many laboratories, however, where there is a set of ordinary burettes in daily use, the cost of the new instruments properly fitted prohibits their introduction, and much time is lost in consequence.

By means of the little apparatus about to be described ordinary burettes may be rendered self-filling, and thus a burette which has been calibrated and in actual use does not require to be discarded.

It consists, as will be seen from the annexed figure, of a T-tube of such a diameter as will enable it to be fixed by means of a cork (or indiarubber stopper) to the burette. Passing down the T-tube is a narrow tube *A* made by suitably drawing out a piece of wider tube. At *B* this tube *A* is fused to the T-tube, or it may be fixed by means of rubber. The narrow tube is then bent and cut off so that the end just touches the wall of the burette. Connection is made with the syphon tube from the stock bottle by means of a rubber tube at *c*.

This tube is provided with a pinch-cock, which, when open, allows the standard solution to flow down the walls of the burette, air bubbles being thus avoided. The displaced air escapes by the side branch of the T, and when the burette is in use air enters at the same place. When the work is finished for the time being, this tube is closed by a piece of rubber carrying a glass plug, or by a small rubber teat.



* From the *Journal and Proceedings of the Royal Society of N. S. Wales*, xxxviii. p. 418.

The apparatus is being made by Messrs. Baird and Tatlock, 45, Renfrew Street, Glasgow, who send it out with the narrow tube straight so that the purchaser may bend it to suit a particular burette.

Chemical Laboratory,
The Technical College, Paisley, N.B.

SOLUTION: FRACTIONAL EXTRACTION.

By PHILIP BLACKMAN.

If a substance is soluble in two liquids which are themselves immiscible, then more of the substance by weight dissolved in one of the liquids can be extracted from the solution by using the other liquid in portions than by employing it all in one extracting operation. The molecular weight of the substance is supposed to be the same in both liquids.

Let W = weight of the dissolved substance,

v_1, v_2 = volumes of the extracting liquid and of the solvent respectively,

s_1, s_2 = coefficient of solubility of the substance in the respective liquids.

1. If the operation of extraction be performed by using the total volume, v_1 , of the liquid, then, if w = weight of solute extracted, $W - w$ = weight of solute remaining, and $w/(W - w) = v_1 s_1 / v_2 s_2$ or $w + w \cdot v_1 s_1 / v_2 s_2 = W \cdot v_1 s_1 / v_2 s_2$. Hence—

$$w = \frac{v_1 s_1}{v_2 s_2} W / \left(1 + \frac{v_1 s_1}{v_2 s_2} \right) \dots \dots \dots 1.$$

2. If the extracting process be performed in n operations, using each time the volume v_1 of the extracting liquid, then the successive weights, $w_1, w_2, w_3 \dots$, of the solute extracted will be—

$$w_1 = v_1 s_1 (W - w_1) / v_2 s_2,$$

$$w_2 = v_1 s_1 (W - w_1 - w_2) / v_2 s_2,$$

$$\dots \dots \dots$$

$$w_n = v_1 s_1 (W - w_1 - w_2 - \dots - w_{n-1}) / v_2 s_2;$$

and the total weight extracted in the n operations—

$$= w_1 + w_2 + w_3 + \dots + w_n =$$

$$= \frac{v_1 s_1}{v_2 s_2} (nW - nw_1 - [n-1]w_2 - [n-2]w_3 - [n-3]w_4 - \dots - w_n) =$$

$$= \frac{v_1 s_1}{v_2 s_2} W - \frac{v_1 s_1}{v_2 s_2} (w_1 + w_2 + w_3 + \dots) +$$

$$+ \frac{v_1 s_1}{n \cdot v_2 s_2} (w_2 + 2w_3 + 3w_4 + \dots).$$

Hence—

$$(w_1 + w_2 + w_3 + \dots) + \frac{v_1 s_1}{v_2 s_2} (w_1 + w_2 + w_3 + \dots) =$$

$$= \frac{v_1 s_1}{n \cdot v_2 s_2} (w_2 + 2w_3 + 3w_4 + \dots) + \frac{v_1 s_1}{v_2 s_2} W.$$

Therefore—

$$w_1 + w_2 + w_3 + \dots = \text{total weight extracted} =$$

$$= \frac{v_1 s_1}{v_2 s_2} W / \left(1 + \frac{v_1 s_1}{v_2 s_2} \right) +$$

$$+ \frac{v_1 s_1}{n \cdot v_2 s_2} (w_2 + 2w_3 + 3w_4 + \dots) \left(1 + \frac{v_1 s_1}{v_2 s_2} \right) \dots \dots 2.$$

Equation 2, it will be observed, is greater than Equation 1 by the quantity $\frac{v_1 s_1}{n \cdot v_2 s_2} (w_2 + 2w_3 + 3w_4 + \dots) / \left(1 + \frac{v_1 s_1}{v_2 s_2} \right)$, which proves the above statement.

East London Technical College,
London, E.

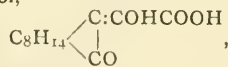
CONDENSATION COMPOUNDS OF CAMPHOR- OXALIC ACID AND AMINES.*

SEVENTH COMMUNICATION ON CAMPHOROXALIC
DERIVATIVES.†

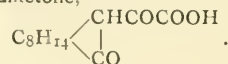
By J. BISHOP TINGLE, Ph.D., F.C.S.,
and
WILLIAM EDWIN HOFFMAN, Jun., Ph.D.

THEORETICAL.

THE investigations carried out by J. Bishop Tingle and his co-workers have shown almost conclusively that the condensation compound of camphor and ethyl oxalate, which has been termed camphoroxalic acid, is an unsaturated keto-alcohol,—

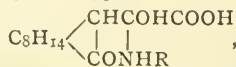


and not the 1,3-diketone,—

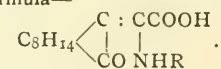


In the course of the work, a new class of compounds was discovered, formed by the condensation of the acid with amines (*Journ. Am. Chem. Soc.*, 1901, xxiii., 363).

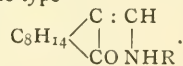
The condensation compounds of the sodium and potassium salts of camphoroxalic acid and of the ethyl ester with amines, both aliphatic and aromatic, were studied. The primary products in all cases were apparently additive substances of the general type—



but only one compound with this formula could be isolated. It was obtained from hydroxylamine and sodium camphoroxalate; the other substances appeared to be unstable and eliminated the elements of water, giving rise to products of the general formula—



Compounds of this nature were prepared from ammonia, hydroxylamine, semicarbazine, aniline, and α - and β -naphthylamine. Such substances as those formulated above might be expected to undergo further change; carbonic anhydride might be evolved with the formation of a compound of the type—



In addition to the above, a third compound of the amine with camphoroxalic acid might be formed, namely, a salt of the acid mentioned above; this would be represented by the formula—



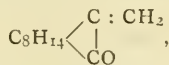
Representatives of these various types were actually prepared from aniline and sodium camphoroxalate. The first by the action of the constituents in a neutral solvent, at the ordinary temperature; the second by the action of aniline and camphoroxalic acid, under pressure at 130°, or by heating the first compound above its melting-point. The third derivative was obtained by the action of aniline on free camphoroxalic acid in a neutral solvent at the ordinary temperature.

In naming these compounds the simplest and most

* From the *American Chemical Journal*, xxxiv., No. 3.

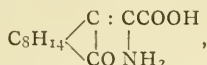
† The previous papers on this subject are as follows:—Inaug. Diss., Munich, 1889, p. 34; *Journ. Chem. Soc.*, 1890, lvii., 652; *Am. Chem. Journ.*, 1897, xix., 393; 1898, xx., 318; 1899, xxi., 236; 1900, xxiii., 214; *Journ. Am. Chem. Soc.*, 1901, xxiii., 363.

advisable method appeared to be to regard them as derived from the complex—

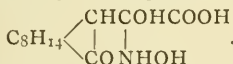


for which the term camphoformene was suggested; it is self-explanatory, and indicates the presence of the double linkage.

By the action of ammonia on sodium or potassium camphoroxalate, sodium or potassium camphoformene-aminecarboxylate was obtained, from which the free acid—

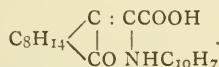


was isolated. Sodium camphoroxalate combines with hydroxylamine, forming the compound—



Semicarbazine unites with potassium or sodium camphoroxalate under the same conditions as hydroxylamine. The products were thought to consist of two compounds having apparently the same empirical formula, but differing in their behaviour towards solvents.

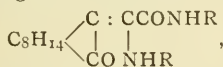
α -Naphthylamine reacted with sodium camphoroxalate under somewhat similar conditions to aniline, and formed α -naphthylcamphoformeneaminecarboxylic acid. The corresponding derivative of β -naphthylamine was also obtained:—



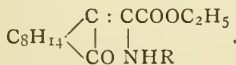
The interaction of orthophenylenediamine and sodium camphoroxalate produced camphoquinoxaline, $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2$.

ETHYL CAMPHOROXALATE DERIVATIVES.

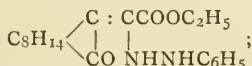
Methylamine, ethylamine, semicarbazine, aniline, and ammonia condensed with ethylcamphoroxalate to form compounds of the general formula—



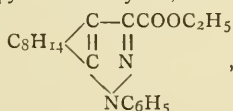
while with aniline or β -naphthylamine the product has the formula—



Phenylhydrazine reacted with ethyl camphoroxalate, forming—



when this was heated above its melting-point, ethyl camphylphenylpyrazolcarboxylate,—

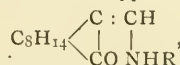


results, and on hydrolysing this compound the free acid was obtained.

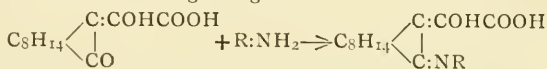
Condensation compounds could not be isolated from ethyl camphoroxalate or sodium camphoroxalate with para- and metaphenylenediamine, ethylaniline, and dimethylaniline.

The object of the present investigation was to determine, if possible, what action would take place between the free camphoroxalic acid and aliphatic and aromatic amines; to ascertain, as far as we were able, the limits within which the condensation takes place; to endeavour to find the cause of the inhibition of the reaction with some

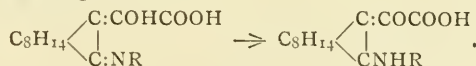
amines, whether it was due to stereometrical influences, to the aliphatic or aromatic nature of the amine, or to its more or less strongly developed positive properties; and to try to discover the conditioning factors for the production of substances of the varying types referred to in the preceding pages. The action of camphoroxalic acid upon a number of metallic compounds was also investigated, and the typical salts of camphoroxalic acid described below have been prepared and analysed. Finally, we desired to investigate the action of acylhalides or substituted acylhalides upon compounds of the type—



the object being to endeavour to obtain evidence of the existence in these compounds of the group R_2NH . Although the behaviour of hydroxylamine and phenylhydrazine towards ethyl camphoroxalate, which has already been referred to, makes it highly probable that the amine attacks the group $>\text{COH}$, yet the possibility of the carbonyl group of the camphor nucleus first reacting with the amine must also be recognised; this, however, would involve the following changes:—



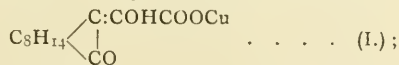
—that is, the $:\text{C}:\text{OH}$ group would remain intact, and should be capable of recognition as such, but this was not found to be the case. The alternative suggestion is that intramolecular rearrangement might take place, and result in the change—



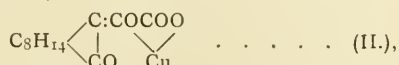
At present there is no evidence in support of this latter view, while the fact that, apart from the salt-forming action of the carboxyl group, camphoroxalic acid combines with amines in equimolecular proportion, would appear to be decisively against it.

METALLIC SALTS OF CAMPHOROXALIC ACID.

When copper nitrate is allowed to react with camphoroxalic acid in a solution of 50 per cent alcohol, at ordinary temperatures, a greenish crystalline mass is obtained, which melts and decomposes at 275° , and has the formula $\text{C}_{12}\text{H}_{14}\text{O}_4\text{Cu}$. The product is the same, irrespective of the proportions in which the copper nitrate and acid are mixed. Two views are possible of the constitution of this salt: if the copper is present in the cuprous condition, it would be—



if in the cupric state, the formula—



would apply, and analysis could, of course, not distinguish between them. At first sight, Formula I., where the carboxyl group only is affected, would seem to be the more probable, and this view might be thought to derive support from the observation that, when the salt is heated in alcoholic solution at 100° , cuprous oxide is deposited. The view that the salt is represented by Formula II. is based upon the following facts:—Its green colour is characteristic of the cupric but not of the cuprous state. In solution the salt fails to give any indication of the presence of copper ions—which behaviour is entirely in accordance with Formula II. Moreover, unlike the barium salt described below, this one gives no colouration with ferric chloride and alcohol, indicating that a change has taken place in the $:\text{COH}$ group of the camphoroxalic acid. The decomposition on heating at 100° is doubtless

solution of nitrates was precipitated with caustic soda, and the hydroxides were washed several times by decantation with boiling water. A warm aqueous solution of chromic acid was then added, and the whole left for several days. A heavy, yellowish white precipitate remained, which, on ignition at a gentle heat, yielded cerium sesquioxide as an almost white powder without the slightest tinge of red or yellow. When thus obtained, the oxide dissolved readily in boiling hydrochloric acid, and the solution, even when viewed through a considerable thickness, did not show a trace of absorption bands.

This last method will be further studied. A chromic-acid method was formerly devised by Pattinson and Clarke (CHEMICAL NEWS, 1867, xvi., 259), but the process is entirely different from the foregoing, and has the disadvantage of giving a ceric oxide which is absolutely insoluble in acids.

15. "A Synthesis of Aldehydes by Grignard's Reaction." By GORDON WICKHAM MONIER-WILLIAMS.

Gattermann and Maffezzoli (*Ber.*, 1903, xxxvi., 4152) showed that aldehydes could be obtained by the action of organo-magnesium compounds on ethyl formate, $\text{H}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_2\text{H}_5 + \text{MgX} = \text{C}_2\text{H}_5\cdot\text{O}\cdot\text{MgI} + \text{X}\cdot\text{CHO}$. and various other investigators have carried out analogous syntheses with derivatives of ethyl formate; for example, bromoform, iodoform, ethyl orthoformate, disubstituted formamides, and isonitriles. The author has shown that ethoxymethylenedianiline, $\text{C}_6\text{H}_5\cdot\text{N}:\text{CH}\cdot\text{O}\cdot\text{C}_2\text{H}_5$, reacts readily with organo-magnesium compounds to give the anhydro-compound of aniline with the aldehyde in question, from which the latter is easily obtained. The yields are in many cases far better than those given by the older methods. Ethoxymethylenedianiline was prepared by the action of ethyl iodide on the silver derivative of formanilide, $\text{C}_6\text{H}_5\text{N}:\text{CH}\cdot\text{OAg}$ (Comstock and Kleeberg, *Am. Chem. Journ.*, 1890, xii., 497), and was allowed to react in absolute ethereal solution at 35° on organo-magnesium compounds. Benzaldehyde, *o*-tolualdehyde, α - and β -naphthaldehydes were obtained from the respective bromo-compounds with yields of 46, 54, 48, and 36 per cent respectively. Some derivatives of β -naphthaldehyde were prepared and analysed, notably β -naphthylacrylic acid, $\text{C}_{10}\text{H}_7\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, and dinitro- β -naphthaldehyde, $\text{C}_{10}\text{H}_5(\text{NO}_2)_2\cdot\text{CHO}$. The method was then applied to the synthesis of a new aldehyde, *p*-thiophenetylaldehyde, $\text{C}_2\text{H}_5\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$. *p*-Nitrothiophenetole (Blanksma, *Rec. Trav. Chim.*, 1901, xx., 403) on reduction gave *p*-thiophenetidine, $\text{C}_2\text{H}_5\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, a slightly yellow liquid boiling at 280° . Its acetyl derivative is thiophenacetone, which, however, does not exert the physiological action of phenacetone. The base was successively converted into the iodo-compound, $\text{C}_2\text{H}_5\text{S}\cdot\text{C}_6\text{H}_4\text{I}$, a slightly yellow oil boiling at 146° 11 m.m., and the aldehyde, $\text{C}_2\text{H}_5\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, boiling at 245° . Several derivatives of the latter were prepared, of which the azine is very characteristic. The oxidation of the aldehyde with alkaline permanganate gave rise to a sulphonecarboxylic acid, $\text{C}_2\text{H}_5\text{S}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H}$.

16. "The Action of Ultra-violet Light on Moist and Dry Carbon Dioxide." By SAMUEL CHADWICK, JOHN EDWIN RAMSBOTTOM, and DAVID LEONARD CHAPMAN.

By the action of ultra-violet light on dry carbon dioxide, the authors have succeeded in partially decomposing carbon dioxide into carbon monoxide and oxygen. The circumstances of the experiment rendered it impossible to decide what percentage of the oxygen was present in the form of ozone. If the carbon dioxide is moist there is no decomposition. The peculiar influence of water vapour is believed to be due to the action which it exerts on the vibrations of the electrons of atoms of which the molecules of carbon monoxide, carbon dioxide, and oxygen are composed. The facts, discovered by Chapman and Burgess, concerning the induction period of a mixture of chlorine and hydrogen are regarded as confirming this view.

17. "A Contribution to the Study of Stable Diazo-compounds." (Preliminary Note). By GILBERT THOMAS MORGAN and WILLIAM ORD WOOTTON.

p-Aminobenzanilide, which has been shown to give on diazotisation a stable diazo-carbonate and a corresponding nitrite (*Trans.*, 1905, lxxxvii., 938), also furnishes a diazonium picrate, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_3)_3$, which is precipitated even in the presence of hydrochloric acid. This substance, which is insoluble in water and crystallises from warm alcohol in rosettes of yellow needles decomposing at 132° , does not explode on percussion. When dissolved in aqueous caustic soda and added to alkaline β -naphthol, it yields a precipitate of benzoyl-*p*-aminobenzeneazo- β -naphthol. Mercury acetamide has been found to yield sparingly soluble, stable additive compounds when added to the aqueous solution of a diazonium salt, and a series of these substances is under investigation. The compound with benzenediazonium chloride gave, on analysis, $\text{N} = 12.46$, whereas $\text{C}_6\text{H}_5\cdot\text{N}_2\text{Cl}\cdot\text{Hg}(\text{NH}\cdot\text{CO}\cdot\text{CH}_3)_2$ requires $\text{N} = 12.26$ per cent. Similar stable mercury acetamide derivatives have been obtained from the substituted anilines and their homologues.

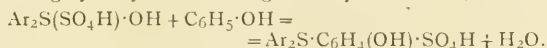
18. "Triarylsulphonium Bases." By SAMUEL SMILES and ROBERT LE ROSSIGNOL.

Quite recently Kehrman and Duttenhöfer have published a paper (*Ber.*, 1905, xxxviii., 4197) dealing with mono- and di-arylsulphonium bases, and, although their work does not clash with that of these investigators, the authors considered it desirable to communicate the following preliminary note to the Society.

It has been found that triarylsulphonium bases can be prepared in three ways.

1. By the action of thionyl chloride on a phenol or phenolic ether in presence of aluminium chloride.
2. By the action of a sulphinic acid on a phenolic ether in presence of concentrated sulphuric acid.
3. By the condensation of an aromatic sulfoxide with phenols or their ethers.

It can be shown that sulfoxides are formed during the first and second reactions, and hence the third reaction may be regarded as the final stage of the first two. The condensation between sulfoxide and phenol takes place with acid condensing agents, and it is the authors' view that the sulfoxide, being basic in character, first forms a salt $\text{Ar}_2\text{S}(\text{SO}_4\text{H})\cdot\text{OH}$, which then reacts with the phenol, losing hydroxyl, and forming the sulphonium salt, thus:—



This reaction seems to be reversible, and a slight excess of phenol must be present to render the conversion of sulfoxide to sulphonium salt complete. At present only the hydroxy- and ethoxy-derivatives have been examined, but the authors hope to extend the investigation to amide and other compounds.

19. "An Improved Apparatus for the continuous Extraction of Liquids with Ether." By RICHARD SISSON BOWMAN.

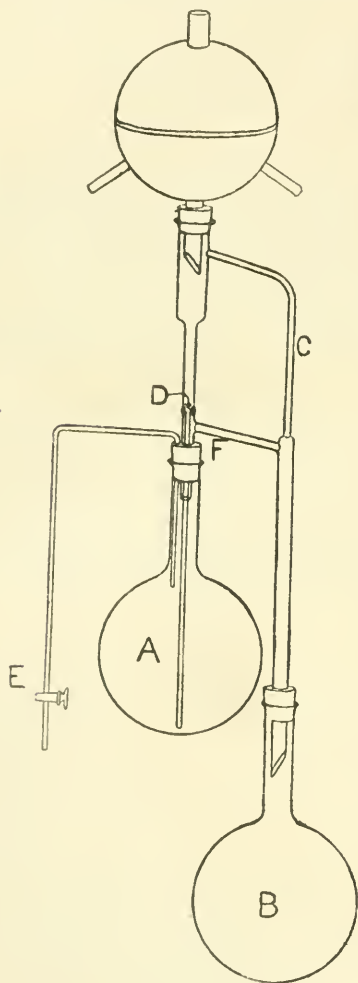
The apparatus here described differs essentially from those due to Hagemann (*Ber.*, 1893, xxvi., 1975), Pellizza (*Chem. Centr.*, 1904, i., 851), and Mameli (*Chem. Centr.*, 1905, ii., 106). In the latter, hot ether vapour is blown through the liquid to be extracted, whilst in the former the extraction is effected by passing cool liquid ether through the solution. Violent bubbling is thus avoided, together with the consequent risk of carrying over mechanically into the ether flask some of the liquid to be extracted.

The apparatus comprises a simple system of tubes, a condenser, and two ordinary flasks, preferably round bottomed.

The liquid to be extracted is placed in the flask A in sufficient quantity to very nearly fill the flask to the bottom of the neck. This flask may frequently be replaced with advantage by a wide test-tube. From one-eighth to one-fifth of this volume of ether, with which the substance is to

be extracted, is placed in the flask B, which is heated on a water-bath or electric heater. The ether passing as vapour up tube C is condensed in the condenser, and falls back and collects in the inner tube, D. A column presently accumulates in D long enough to force its way through the liquid in A, and there is then a constant succession of small drops of ether ascending in A, collecting on the surface of the liquid, and finally overflowing at F and returning to the flask B.

On completion of the process of extraction, the neck of the flask will be filled with ether. There will also be a column of ether in tube D, reaching a few centimetres above tube F, and hence the neck of the flask may be emptied by opening the stopcock E and allowing the ether to run off into some vessel. If necessary, the flask may now be replaced by a similar one containing a fresh portion of the liquid to be extracted, and the process resumed.



Among other advantages claimed for this apparatus are that, whereas the other forms involve either expert glass-blowing or innumerable cork and indiarubber joints, it is simple in construction, and may easily be made by anyone moderately skilled in the use of the blowpipe. It is very easy to keep clean and convenient to charge, since the vessels which contain the liquid to be extracted and the extracting liquid are ordinary flasks. A large quantity of liquid, moreover, may be rapidly and completely extracted with the use of a very small quantity of ether.

Benzene, ligroin, or any other suitable solvent may be used with equal ease, provided it is immiscible with water and of lower specific gravity than the liquid which it is to be used to extract.

Ordinary Meeting, February 1st, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MR. J. B. TILLOTT was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Roderick Harold Capper Birt, B.A., 54, Shooter's Hill Road, Blackheath, S.E.; William Dickson, Branksome, Bridge of Weir; James Stuart Hills, Oxford Street, W.; Ernest Ormerod, M.Sc., Ph.D., 8, Leopold Road, Wimbledon, S.W.; John Henry West, 11, Sydney Street, Chelsea, S.W.; Henry John Wiffen, 17, Albany Road, Manor Park, E.

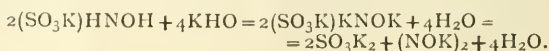
Of the following papers, those marked * were read:—

*20. "Hydroxylamine- $\alpha\beta$ -disulphonates (Structural Isomerides of Hydroximiniosulphates or Hydroxylamine- $\beta\beta$ -disulphonates)". By TAMEMASA HAGA.

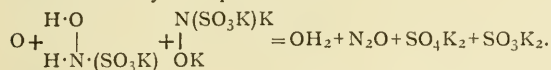
In a previous paper (*Trans.*, 1904, lxxxv., 78; *Proc.*, 1903, xix., 281), it was shown that Fremy's *metasulphazilates* are *hydroxylaminetrisulphonates*. From these salts there has now been obtained by hydrolysis a new series of salts which are structurally isomeric with Fremy's *neutral* and *basic sulphazotates*, now known to be *hydroxylaminedisulphonates*. The new salts are decomposed by sodium amalgam, and are proved by the nature of this change, by their decomposition by concentrated potassium hydroxide solution, and by their hydrolysis, to be *hydroxylamine- $\alpha\beta$ -disulphonates*, in contrast with the *sulphazotates*, which are *hydroxylamine- $\beta\beta$ -disulphonates* $\text{SO}_3\text{K}\cdot\text{ONH}\cdot\text{SO}_3\text{K}$ and $\text{HON}(\text{SO}_3\text{K})_2$, respectively. This is believed to be the first indisputable case of the occurrence of fundamental structural isomerism among inorganic compounds. Sodium converts the new salts into sulphate and aminemonosulphonate; potassium hydroxide into the same products, together with nitrogen; and acids transform them into sulphate and hydroxylamine. The new salts are practically all soluble in water and fairly stable; those prepared are principally the di- and tri-potassium salts, di- and tri-sodium salts, and the di-ammonium salt. A *hydroxylamine- α -monosulphonate* seems incapable of existence; it would be, for example, a sulphate of potassium and amidogenium, $\text{H}_2\text{NO}\cdot\text{SO}_2\cdot\text{OK}$.

DISCUSSION.

Dr. DIVERS said that it follows somewhat unexpectedly from the author's results that it is the presence of oxylic hydrogen and not aminic hydrogen in a hydroxylamine derivative or in hydroxylamine itself which makes it easily oxidisable. For, whilst a hydroxylamine- $\alpha\beta$ -disulphonate is not sensitive to oxidising agents, although it contains an atom of aminic hydrogen, a hydroxylamine- $\beta\beta$ -disulphonate which contains none is readily oxidised to a peroxylamine-sulphonate (*Trans.*, 1904, lxxxv., 78; *Proc.*, xix., 281) by virtue of the oxylic hydrogen atom, which is present in it but not in the $\alpha\beta$ -salt. Applying this deduction from facts to the case of the very sensitive hydroxylaminemonosulphonates, an explanation is found for the fact that these salts, when oxidised, as by cupric chloride or by cupric oxide in alkaline solution (*Trans.*, 1889, lv., 760), give nitrous oxide but no hyponitrite, although when decomposed by potassium hydroxide alone they give much hyponitrite, together with sulphite. The production of hyponitrite by alkali alone is represented by—



Its non-production, when cupric oxide is also present, is accounted for by the equation:—



(Copper sulphate induces oxidation of a hydroxylamine-monosulphonate catalytically, causing one-half of it to be reduced to aminemonosulphonate in oxidising the other half in the way just formulated. Compare *Trans.*, 1900, lxxvii., 978).

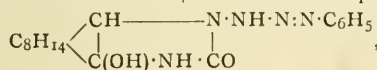
It should therefore be taken into consideration, when determining the constitution of organic and other substitution derivatives of hydroxylamine, that indifference to oxidising agents is not evidence of the absence of aminic but of oxylic hydrogen.

He also suggested, in explanation of the fact that a small part of a hydroxylamine- $\alpha\beta$ -disulphonate is much more difficult to hydrolyse than the rest, that the salt may polymerise to some extent during the heating, and thus become resistant to hydrolysis.

In reference to the circumstance that some of the author's results had been anticipated by Raschig (*Ber.*, 1906, xxxix., 245), and the question of dating communications have been raised by Prof. McLeod, Prof. ARMSTRONG expressed the hope that no alteration in the existing practice would be made, and that nothing would be done to deprive authors of the liberty which they had so long enjoyed of correcting their papers up to the moment of publication. It was most undesirable that anything should be done to encourage discussions as to priority among authors. The public were gainers, when, as in the present case, independent workers arrived at similar results.

*21. "Studies in the Camphane Series. Part XXI. Benzenediazo- ψ -semicarbazinocamphor and its Derivatives." By MARTIN ONSLOW FORSTER.

When a diazonium salt is added to an aqueous solution of camphoryl- ψ -semicarbazide nitrate, the corresponding derivative of benzenediazo- ψ -semicarbazinocamphor,—



is precipitated. Compounds of this class may be called diazo- ψ -semicarbazines, and have been obtained from diazotised aniline, *p*-toluidine, *p*-anisidine, *p*-chloroaniline, *p*-bromoaniline, and the three nitroanilines; they are characterised by the readiness with which dilute alkalis resolve them into camphoryl- ψ -carbamide and the corresponding phenylazoimide. The author dissented from the views on coloured camphor derivatives expressed by Armstrong and Robertson (*Trans.*, 1905, lxxxvii., 1272).

DISCUSSION.

In replying to Dr. Forster, Prof. ARMSTRONG said that, beyond remarking that Stobbe's results were in no way irreconcilable with his (the speaker's) views as to the origin of colour, as he proposed to consider them on another occasion, he should not deal with them then; nor would he continue the discussion on the relation of optical activity to structure in hydrazones, as this subject could not be dealt with properly in the time at disposal. He would confine his remarks to the compounds described by Dr. Forster. Of the two alternative formulæ available for the semicarbazines, Dr. Forster had selected that containing the group $\cdot\text{N}\cdot\text{NH}\cdot\text{N}\cdot\text{NPh}$. Inasmuch as compounds containing the group $\cdot\text{N}\cdot\text{NPh}$ were at least yellow, he was of opinion that the formula selected did not represent the colourless compounds. He was of opinion also that, although prepared by one method, Dr. Forster's compounds were not all of one type, any more than *o*- and *p*-nitrophenol and nitraniline were compounds of the same type as the corresponding bromophenols and bromanilines. It had long been admitted that the nitro-compounds referred to are at least partially composed of the isodynamic

quinonoid forms; the differences observed by Dr. Forster between his colourless and coloured compounds were precisely those observed on comparing the bromanilines with the nitranilines.

Dr. LANDER remarked that it was unlikely that nitrogen compounds of this type would exhibit tautomerism. Pechmann had shown that the so-called "virtually tautomeric" mixed amidines were mixtures or "solid solutions" of structural isomerides, and further that the isomerism disappeared when the hydrocarbon residues were of different types, as in Dr. Forster's compounds.

Dr. LOWRY said that Dr. Forster appeared to have overlooked the fact that one of Stobbe's compounds, the phenyldimethylfulgide (*Ber.*, 1905, xxxviii., 3895) existed both in a yellow and in a colourless form, the two forms being convertible into one another in much the same way as the isomeric white and yellow oximes of the mesoxamide series studied by Dr. Whiteley (*Trans.*, 1903, lxxxiii., 24). There was, therefore, the clearest possible evidence of the existence of dynamic isomerism in Stobbe's series of compounds, and the argument that individual members of such a series must have the same constitution because prepared in the same way and exhibiting similar chemical properties was entirely fallacious.

Dr. MORGAN cited the case of the ortho-diazoimines as another example of a group of compounds the members of which series differed considerably in colour although they were all prepared by the same general method and had similar properties. Diazoiminobenzene and its acyl derivatives were white or colourless substances. 2:3-Diazoiminonaphthalene was described as yellow, whereas 1:8-diazoiminonaphthalene is brownish red. In spite of this colour difference there seemed to be no reason for supposing that these substances were differently constituted.

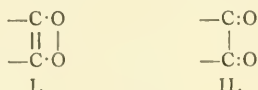
Although three of Dr. Forster's diazo- ψ -semicarbazines were nitro-compounds and possibly owed their colour to the presence of the nitro-group, yet it was very unlikely that the yellow *p*-anisyl derivative should be differently constituted to the white *p*-tolyl compound, inasmuch as the former differed from the latter only in the substitution of methoxyl for methyl in the para-position to the diazo-complex.

Dr. FORSTER, in reply, regretted that Dr. Lowry had misunderstood his attitude. He had not used "the argument that individual members of such a series must have the same constitution because prepared in the same way and exhibiting similar chemical properties." His contention was, that in the absence of chemical distinctions among a series of compounds prepared alike, it was unsafe to say that the structural type of a colourless compound must differ from that of a coloured one merely because the substances differed in appearance. That was his reason for criticising the views of Professor Armstrong and Mr. Robertson regarding the structure of their camphor-quinonehydrazones, and nothing had been said that evening which impaired his conviction that to deduce a certain constitutional formula for a coloured substance solely from the assumption that the colour is due to the constitution ascribed is arguing in a circle, and therefore unacceptable.

*22. "The Relations between Absorption Spectra and Chemical Constitution. Part I. The Chemical Reactivity of the Carbonyl Group." By ALFRED WALTER STEWART and EDWARD CHARLES CYRIL BALY.

Attention has been drawn (*Trans.*, 1904, lxxxv., 1029, and 1905, lxxxvii., 766) to the relation which exists between tautomerism and the selective absorption which is shown by the spectra of derivatives of ethyl acetoacetate, whilst it has also been proved that the rates of addition of sodium hydrogen sulphite to ketones can be influenced by the introduction of a carboxyl radicle into the molecule, and that the effect thus produced is directly opposite to what one would expect if the hypothesis of steric hindrance held good (*Trans.*, 1905, lxxxvii., 185, and *Proc.*, 1905, xxi., 78). In the present paper, it is shown that these two phenomena are connected with one another, and the relation is indicated

between the activity of the carbonyl group in certain ketones and their selective absorption. It is pointed out that in certain cases the phenomena of tautomerism furnish an explanation of the exceptional reactivity of the carbonyl group, as the passage from the enolic to the ketonic form would give rise to a carbonyl radical, the condition of which may be considered as approximating to that of a nascent atom. This "nascent carbonyl group" would be more reactive than the normal carbonyl. But although in most instances tautomerism suffices to explain the phenomena, it breaks down in several cases, and to cover these a new and wider conception is required. From spectroscopic evidence it appears that in the α -diketones a vibration is going on which to a certain extent resembles that which was found in the case of ethyl acetoacetate and its derivatives. The nature of this vibration cannot be easily expressed in the ordinary structural formulae without the possibility of misconception, but it may be indicated somewhat as follows:—The vibration is brought about by some change in the relations between the carbon and oxygen atoms, and it in some respects resembles the transition from the ketonic to the enolic form and back again. Using this analogy, we may postulate that the two extreme phases of the vibration can be represented by the formulae:—



The conversion of I. into II. would give rise to the "nascent carbonyl group" just as the change of the enolic into the ketonic form does. Further, the experimental evidence available shows that some such relation does actually exist between the carbonyl groups of benzoquinone, and the great reactivity of the quinones can be thus explained. It is proposed to term the general phenomenon "*isorropesis*," and to call "*isorropic*" those radicals the activity of which is thus produced.

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Meeting held at Burlington House on February 5th, 1906.

"Carburetted Water-gas in the Bunsen Burner." By MATSUMI CHIKASHIGE.

In a previous paper (*Journ. Soc. Chem. Ind.*, 1904, 50) H. Matsumoto and the author pointed out the defects of water-gas as a fuel in the chemical laboratory. Carburetted water-gas is now prepared in the Kyoto University by injecting heavy petroleum oil with steam into a water-gas generator filled with ignited coke. The gas produced is passed through a superheater loosely packed with fire-bricks, and then through a scrubber, after which treatment it enters the gas-holders. The mean composition of the gas differs little from that of coal-gas, and the products of combustion closely resemble those of coal-gas.

To obtain the usual flame of a Bunsen burner (15 c.m. long) a flow of 120 litres of coal-gas, 300 of water-gas, and 120 of carburetted water-gas are required; therefore the triangular orifice of the ordinary Bunsen burner for coal-gas requires to be only slightly enlarged to get the same sized flame with the carburetted water-gas.

The carburetted gas has no effect on the ordinary laboratory vessel, and the products of combustion, unlike those of plain water-gas, are not more injurious in insufficiently ventilated laboratories than those of coal-gas.

"The Loss of Nitre in the Chamber Process." By J. K. H. INGLIS.

The loss of nitre, which amounts in many works to about 3 per cent of the sulphur burnt, can best be traced by complete analyses of the flue gases in which the quantity

of nitre, calculated as nitric oxide, should amount to about one part in one thousand by volume. The analysis of these gases cannot be carried out by means of aqueous absorbents owing to the formation of complicated bodies by the interaction of nitrous acid and sulphur dioxide. But the whole analysis can be carried out very conveniently by the fractional distillation of the gases, first at the temperature of liquid air, and subsequently at higher temperatures. The results showed that only about 4 per cent of the lost nitre was lost as nitrous oxide, and that as a mean of eight experiments the loss as nitrogen peroxide amounted to about 43 per cent of the total loss. In the first experiments the temperature was not sufficiently low to effect the separation of nitric oxide from the flue gases, since at the temperature of liquid air the vapour pressure of nitric oxide is considerable. Some further experiments were therefore made at a still lower temperature, obtained by making the liquid air boil under diminished pressure. Contrary to expectation, however, the amount of nitrogen oxides found was no greater than that in the earlier experiments; and this might therefore be taken to mean the nitric oxide is not present in the flue gases. These last experiments, however, were not made under quite the same conditions of the plant as the earlier experiments, and further work is needed before one can draw any definite conclusion in regard to the presence of nitric oxide.

"The Removal of Nitrous Acid from Concentrated Nitric and Sulphuric Acid." By O. SILBERRAD and B. J. SMART.

The experiments were carried out at the Royal Arsenal, Woolwich, and communicated with the consent of the Explosives Committee. They were made to determine to what extent the reaction between nitrous acid and amines or amides occurs in concentrated acids. Nitric acid containing a small percentage of nitrous acid was taken either alone or in admixture with sulphuric acid. Various reagents which are known to react readily with nitrous acid in aqueous solution were added to the concentrated acid, and allowed to stand at the ordinary temperature. From time to time the amount of nitrous acid present was determined by titration with permanganate. The addition of hydrazine occasions an explosion, and with this exception substances such as urea, lead peroxide, oxamide, methylamine nitrate, and amido-guanidine, are very inert towards nitrous acid in presence of concentrated nitric acid, although they react readily enough in dilute solution. The observation of Franchimont that urea nitrate decomposes with evolution of carbon dioxide and nitrous oxide was confirmed.

FARADAY SOCIETY.

Ordinary Meeting, January 30th, 1906.

Prof. A. K. HUNTINGTON in the Chair.

The following nominations for the Officers and Council to be elected at the forthcoming Annual General Meeting were announced:—

President—Lord Kelvin, O.M., G.C.V.O., F.R.S.

Vice-Presidents—Prof. A. Crum-Brown, M.D., F.R.S.; Prof. W. Hittorf; Sir William Huggins, O.M., K.C.B., F.R.S.; Sir Oliver Lodge, F.R.S.; Ludwig Mond, Ph.D.; F.R.S.; Lord Rayleigh, O.M., P.R.S.; Prof. J. J. Thomson, F.R.S.

Treasurer—F. Mollwo Perkin, Ph.D.

Council—Bertram Blount, F.I.C.; W. R. Cooper, M.A.; Prof. A. K. Huntington; R. S. Hutton, D.Sc.; Herbert Jackson, M.A.; T. M. Lowry, D.Sc.; W. M. Morrison, M.Inst.C.E.; O. J. Steinhart, Ph.D.; J. Swinburne, M.Inst.C.E.; Prof. E. Wilson.

Mr. W. MURRAY MORRISON read an abstract of a paper presented by ADOLPHE MINET on "*The Electric Furnace*;

its Origin, Transformations, and Applications." (Part III.).

The previous sections of the paper, which is of a classificatory and historical character, dealt with the first or laboratory period of the development of the electric furnace. The second period, inaugurated by the researches of the brothers Cowles, and of Héroult (1886-1887), saw the birth of industrial furnaces, and the beginnings of three new industries—the electrometallurgy of aluminium, the electrometallurgy of sodium, and the preparation of refractory materials. The present paper deals almost entirely with the first of these industries.

The methods for the manufacture of aluminium are divided into two principal groups—the electrothermic methods, which produce the metal alloyed with copper or iron, or combined with carbon, and electrolytic methods, which yield pure aluminium. The furnaces of Cowles, Borchers, and Willson, the early types of the Héroult furnace, and the Minet "mixed" furnace are described, among others, under the former heading. The principal electrolytic furnaces dealt with are those of Héroult, Minet, and Hall, and finally some of the more recent suggested improvements in the electrometallurgy of aluminium are briefly outlined.

Mr. E. RISTORI added some interesting details in connection with the early work of Héroult and others. Kleiner, in 1885, had unknowingly decomposed bauxite, and produced small quantities of aluminium.

Mr. W. M. MORRISON pointed out that Héroult's invention was actually made in 1885, although his patents only dated from 1887.

Dr. O. J. STEINHART referred to recent patents of Hall for purifying bauxite electrolytically, and of Bett for depositing pure aluminium from an impure electrolyte.

Mr. BERTRAM BLOUNT said that, although the purification of the bauxite was the whole crux of the aluminium problem, yet now there might be found uses for impure aluminium in connection with "thermit" welding. He discussed some of the developments that had taken place in the general design of electric furnaces.

Mr. F. W. HARBORD, in reply to a question, said that calcium might, if it could be made cheaper, replace aluminium for getting rid of over-oxidation in steel, but it had not yet been really tried.

Dr. J. A. HARKER then gave a demonstration of a Solid Electrolyte Tube Furnace.

The furnace was designed for uses in which the presence of hydrocarbons or other reducing gases, inseparable from a carbon tube furnace, was undesirable. It has, in particular, been used for calibrating thermo-couples, and determining the melting-point of platinum, which the author gives as 1703—1713° C. The furnace is practically an overgrown Nernst lamp, consisting of a tube made of a mixture of zirconia and 10 per cent yttria, which is squirted through a die and then baked. The small type shown in operation was 2½ in. long between the contacts. When taking one ampère at about 120 volts a temperature of 1600° C. was attained. The tube is made conducting either by heating direct, or else by surrounding it with an external nickel heating coil, separated from it by a layer of pure zirconia, the combination forming a "cascade" type of furnace. Special attention has to be paid to the contact of the platinum leading-in wires and the tube.

With regard to the mechanism of conduction through Nernst conductors, the author thought that a comprehensive and satisfactory theory was at present lacking. It was, however, certain that the conduction was electrolytic, because by pumping away the atmosphere surrounding a Nernst glover, to prevent re-combination, a metallic filament could ultimately be obtained.

Mr. BERTRAM BLOUNT thought no special mechanism was needed to explain solid electrolysis. Ordinary transference of ions would take place in a semi-plastic mass.

Dr. T. M. LOWRY referred the author to the dissertation by Reynolds. The conduction was similar to that which occurred in hot glass.

Mr. E. B. R. PRIDEAUX communicated a paper entitled "Note on the Production of Ozone by Electrolysis of Alkali Fluorides." (See CHEMICAL NEWS, xciii., p. 47).

NOTICES OF BOOKS.

The Nature and Origin of Living Matter. By H. CHARLTON BASTIAN, M.A., M.D., F.R.S., F.L.S. London: T. Fisher Unwin. 1905.

THIS volume contains a full account of Dr. Bastian's views, which are already well known in outline by the scientific world. The author has now brought together a large accumulation of material, which he has been collecting for many years, and he gives minute descriptions of his investigations and observations, fully illustrated by photo-micrographs. A large part of the book is devoted to the consideration of the subject of archæbiosis, and by the experiments described the author believes that he has proved that no logical or consistent reason exists for a disbelief in its present occurrence. Then he passes to Heterogenesis and the Heterogenetic Origin of Bacteria and their Allies, and gives details of many miscellaneous examples of heterogenesis. While every page of the book reveals the writer's talents for investigation, and the excellence of his equipment for work of this nature; nevertheless, it is doubtful whether it will lead to the conversion of many, although through it some may perhaps be brought to recognise at any rate the possibility of the truth of what Dr. Bastian puts forward. Difficult as the facts may be of credence, an open mind must be preserved towards them; but it may be pointed out that a certain weakness is displayed in discussing the interpretation of some of the phenomena observed; for instance, the critical flask experiments. A weak point seems to be the "necessary precautions against infection," and the impossibility of maintaining absolute isolation of the organisms under observation, which, of course, leaves a loophole for explaining away the phenomena. Every one interested in the problem of the origin of life should devote serious and careful study to this book; all new theories must meet with opposition, but the vigour of the opposition is often a measure, not of the falsity of the new hypothesis, but of the depths of our ignorance of some aspect of the subject before it was propounded.

Chemie der Alicyclischen Verbindungen. ("The Chemistry of the Alicyclic Compounds"). By OSSIAN ASCHAN. Braunschweig: Friedrich Vieweg und Sohn. 1905.

THE name suggested by Bamberger for those organic substances which contain a ring nucleus and exhibit the essential characteristics of aliphatic compounds, has been adopted by the author as the most suitable and convenient for the cyclo-paraffins of general formula C_nH_{2n} and their derivatives, excluding naturally the aromatic hydrocarbons; and this is the first book yet published devoted entirely to the study of these substances. The author discusses in it the influence of the ring binding upon both the chemical and physical nature of the compounds and their stereo-chemistry, besides describing in the special part their methods of formation. The alicyclic compounds form a class which is of great importance in organic chemistry, many of the substances being employed technically, and special attention is devoted to such as are of more than purely theoretical interest. These include the camphors, terpenes present in ethereal oils and the naphthenes of petroleum, besides many other naturally-occurring compounds. The author, who has done pioneering work upon the alicyclic series, has also rendered a valuable service to organic chemistry in collecting and arranging systematically all the results which have been obtained in this region.

An Introduction to Volumetric Analysis. By A. JAMIESON WALKER, Ph.D. (Heidelberg), B.A., and OWEN E. MOTT, Ph.D. (Heidelberg). London: Chapman and Hall, Ltd. 1905.

WE have in this little book a useful course of volumetric analysis, presented in such a way as to force the student to think about what he is doing, and to prevent him working mechanically. With this end in view, the authors have as far as possible not given exact directions as to weights and volumes to be used, but simply provided the data necessary for the student to calculate these quantities, and one useful feature is the system of giving many tables of strengths of solutions, left blank to be filled up by the worker. The directions for the experiments seem to be in all cases clear and full, equations are given wherever necessary, and the calculations are explained very carefully. The order in which the subject is attacked hardly seems to be the best possible; it is generally found advisable not to give the student solutions of known strength to work with, but to let him first prepare standard solutions, and, working with them, to determine unknown solutions. This, however, is a criticism which only applies to the first few pages, and it would not be difficult to alter the arrangement of the experiments if it seemed desirable.

Kurzes Lehrbuch der Organischen Chemie. ("A Short Text-book of Organic Chemistry"). By Prof. Dr. A. BERNTHSEN. Ninth Edition. Braunschweig: Friedrich Vieweg und Sohn. 1906.

THE English version of Prof. Bernthsen's "Text-book of Organic Chemistry" has been much used in schools and colleges in this country, and a ninth edition will be heartily welcomed both by students and teachers. Like the eighth, this edition has been prepared in collaboration with Dr. Ernst Mohr, and some important changes have been made in it. For instance, the text is for the first time divided into three parts, a procedure rendered necessary by the growth of our knowledge of compounds belonging to the heterocyclic class formerly treated partly in the chapter on the transition to the aromatic compounds, and partly in the appendix to the benzene derivatives. These heterocyclic compounds now form a large and important class to themselves, while the cyclic polymethylenes are classified together with the benzenes and hexamethylenes as isocyclic substances. With these exceptions the work preserves very much its original form and distinctive character, the excellent summaries and generalisations, which were so greatly to be commended, being still a prominent feature of the book.

The Conductivity of Liquids. By OLIN FREEMAN TOWER, Ph.D. Easton, Penna.: Chemical Publishing Company. 1905.

ONE of the aims of this book, which describes methods, results, chemical applications, and theoretical considerations, is to lead to the more general adoption of the Kohlrausch system of units, and in it the author gives a very clear and concise summary of the work which has been done on the conductivity of liquids. All standard methods are well described, and special attention is paid to transport numbers and the theory of electrolytic dissociation. One valuable portion of the book is devoted to non-aqueous solutions and the conductivity of electrolytes in mixed solvents, both subjects being very lucidly treated.

Académie des Sciences.—At the meeting on the 12th of February the Academy of Sciences elected Sir William Crookes a Correspondent of the Institut (*Académie des Sciences*, General Physics Section), in place of M. Bichat, deceased.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 3, January 15, 1906.

The Component $\cdot\text{C}(\text{OH})$ of Tertiary Alcohols.—Louis Henry.—The $\cdot\text{C}(\text{OH})$ alcohol function resides in the component $\cdot\text{C}(\text{OH})$ of tertiary alcohols, especially in trimethylcarbinol, $(\text{H}_3\text{C})_3\text{C}(\text{OH})$, the perfect type of this class of compounds. The author makes a series of experiments showing how the presence of elements or different radicals attached to the carbon of the component $\cdot\text{C}(\text{OH})$ profoundly modify the functional nature of the hydroxyl—OH alcohol.

Copper Silicide and a New Method of Formation of Silicon Soluble in Hydrofluoric Acid.—Paul Lebeau.—In a previous paper the author showed that the limit of combination of copper and silicon in industrial cupro silicon containing 50 to 60 per cent of silicon never passes 10 per cent, and apparently corresponds to the production of a definite compound having a formula SiCu_4 . He now investigates what is the influence the velocity of cooling has on a molten mixture of copper and silicon. Also the total proportion of silicon at the limit of silicuration, but his results do not admit of the statement of any fixed law. The limit of silicuration, however, does correspond to SiCu_4 .

Thorium Silicide.—O. Hönigschmid.—It was predicted that thorium oxide would be reduced by silicon at the high temperature of the electric furnace. The author makes several attempts by this method, hoping to obtain thorium silicide which had never been prepared. He finds, however, that even with a large excess of silicon a considerable proportion of thorium remains unattacked. The product obtained looks like melted metallic silicon. When treated with potash the excess of silicon can be removed, and a grey powder remains which, examined under the microscope, looks like crystalline fragments and non-reduced oxide. The metallic portion is attacked by all the mineral acids. It is impossible to separate this from the oxide, which only hot concentrated sulphuric acid can dissolve. The use of aluminium, however, will dissolve the silicon without entering into combination with it, and so allows of the preparation of crystalline thorium silicide. There forms at the same time an alloy of thorium and aluminium of a different crystalline form.

Diamine Diazoics.—Léo Vignon.—The author obtains by linkage with aniline a series of new compounds, and enunciates the following law relative to the diazotation of the aromatic diamines:—The diazotation of the two NH_2 groups of the diamines takes place in the same manner as that of the monamines when the NH_2 groups are joined to distinct benzenic radicals. When the two groups are joined to the same radical the diazotation is not effected in the case of the ortho-compound, whilst in the case of the meta- and para-derivatives very unstable diazoic derivatives are formed.

Estimation of Small Quantities of Chloroform (1) in Air, (2) in Blood, or an Aqueous Liquid.—Maurice Nicloux.—The author describes an application of the classic reaction of M. Dumas,—



to the estimation of small quantities of chloroform, avoiding the complication of a sealed tube. In order to estimate the chloroform in the water vapour of the air, this is collected in alcohol, and to apply the same method to the estimation of the chloroform present in blood or an aqueous solution he describes certain modifications.

Estimation of Carbonic Oxide in Air by means of Iodic Anhydride.—Albert Lévy and A. Pécoul.—The authors find that during the important researches on the subject of the combustible gases in air very small traces of carbonic oxide give an intense colouration with starch when acting upon iodic anhydride, whilst 1 volume in 10,000 of acetylene produces no colouration.

Combustion of Acetylene by means of Oxygen.—Paul Mauriceau-Beaupré.—The author finds that in the analysis of industrial atmospheres there are difficulties in the way of combusting the acetylene present with oxygen, and he prefers to utilise MM. Albert Lévy and A. Pécoul's apparatus.

Direct Proportion between the Cryoscopic-point of a Mineral Water of the Bicarbonate Class and the Composition of this Water expressed in Anhydrous Salts and Mono-carbonates.—Lucien Grause.—The author's researches on the cryoscopic of mineral waters allow him to determine in a perfectly definite manner the relation existing between the cryoscopic-point of a mineral water of the bicarbonate class, such as that of Châtel-Guyon, and its composition. The analyses of mineral waters generally are usually reduced to bicarbonates, and there apparently exists no relation in the ordinary way between the total of their mineral matter and their cryoscopic-points. However, he definitely proves that if in the case of bicarbonate waters their composition is expressed in anhydrous salts and mono-carbonates there is a direct proportion between the cryoscopic-point and the composition.

MISCELLANEOUS.

On Anti-friction Metals.—Sergius Kern, M.E., St. Petersburg.—In the *CHEMICAL NEWS*, No. 2410 (xciii., p. 47), was inserted my note on anti-friction metals. I use the results of my experiments as a method for testing various babbitts for engineering purposes. For instance, engine-bearings for high tensions demand babbitts with high melting-points. Now, if a choice must be made from different brands of anti-friction metals, the latter having a smaller interval between their melting- and freezing-points, must be preferred as showing more homogeneity in the metal.—February 11th, 1906.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Miss Ruddle Browne, Dr. G. L. Findlay, Miss M. H. Pamm, Mr. A. Sutton, Mr. L. C. Wallach, and Miss I. K. Young were elected Members. The Special Thanks of the Members were returned to Dr. Hugo Müller, F.R.S., for a donation of £100, to Professor J. A. Fleming, F.R.S., for a donation of £25, and to the Rev. J. H. Ellis, M.A., for a donation of £25 to the Fund for the Promotion of Experimental Research at Low Temperatures.

MEETINGS FOR THE WEEK.

MONDAY, 19th.—Society of Arts, 8. (Cantor Lectures). "Modern Warships," by Sir William White, F.R.S., &c.
TUESDAY, 20th.—Royal Institution, 5. "Food and Nutrition," by Prof. William Stirling, M.D., &c.
— Society of Arts, 8. "Illuminated Manuscripts," by H. Yates Thompson, F.S.A.
WEDNESDAY, 21st.—Society of Arts, 8. "The Fisheries of the North Sea," by Walter Garstang M.A.
— Microscopical, 8. "Improved Method of taking Stereophotomicrographs and of Mounting the Prints," by H. Taverner. Exhibition of Oribatida, presented by N. D. F. Pearce.
THURSDAY, 22nd.—Royal Institution, 5. "The English Stage in the Eighteenth Century," by H. B. Irving, M.A.
FRIDAY, 23rd.—Royal Institution, 9. "The Internal Architecture of Metals," by Prof. J. O. Arnold.
SATURDAY, 24th.—Royal Institution, 3. "George Frederick Watts, as a Portrait Painter," by M. H. Spielmann.

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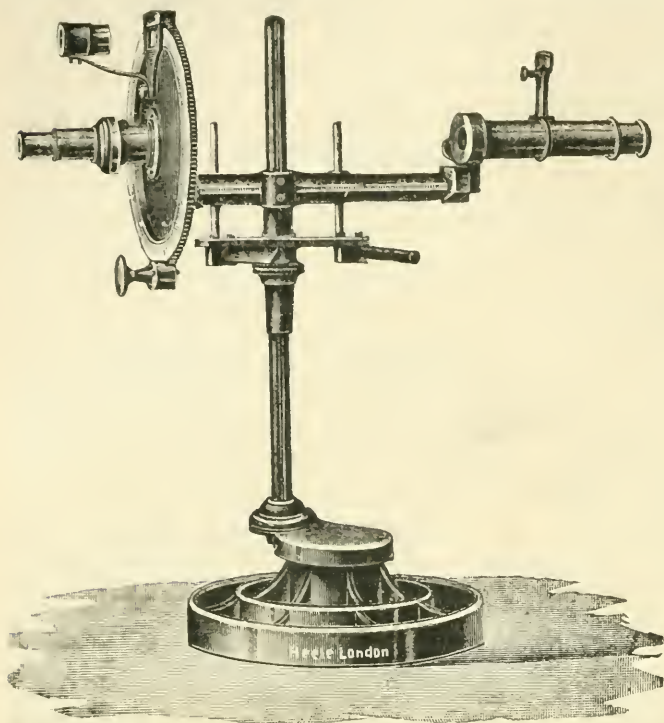
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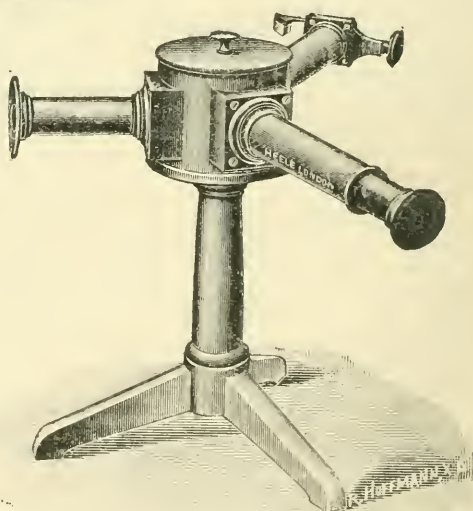
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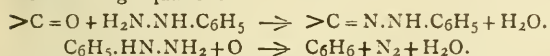
QUANTITATIVE DETERMINATION OF THE CARBONYL GROUP IN ALDEHYDES, KETONES, &c.

MODIFICATION OF THE STRACHE METHOD.

By WATSON SMITH, Jun.

IN seeking to minimise certain inconveniences in H. Strache's method of estimating quantitatively the carbonyl group,* it was found that the following modifications considerably improved the process.

The method as to theory remains exactly the same, and consists in mixing the aldehyde or ketone with excess of phenylhydrazine; the excess is then oxidised by boiling with Fehling's solution, and the nitrogen gas liberated is collected and measured. The reactions are expressed in the following equations:—

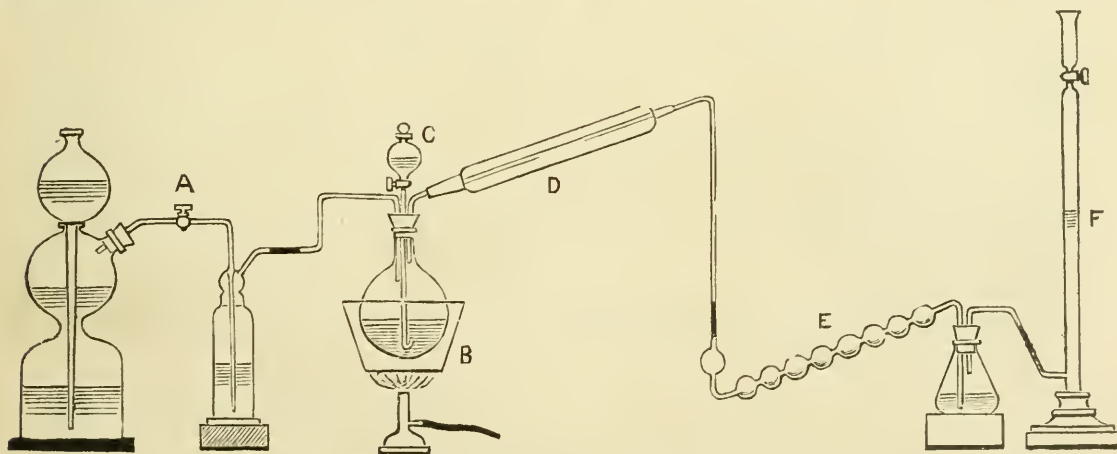


The alterations in the process concern more especially the collection and estimation of the nitrogen gas.

The aldehydic or ketonic substance under examination (0.1 to 0.5 grm.) is mixed with an accurately measured quantity of the phenylhydrazine solution (1 part), and the sodium acetate solution (1½ parts) in a 100 c.c. measuring flask. Water is added to the mixture so as to make the volume up to about 50 c.c., and the liquid then heated on the water-bath for about fifteen minutes. After cooling, it is diluted to the 100 c.c. mark, well shaken, and the determination continued as follows:—

A stream of well washed carbon dioxide is led from the Kipp's apparatus into the flask B (see Fig.), which has a capacity of 750 to 1000 c.c., and contains 200 c.c. of Fehling's solution, on the surface of which floats a thin layer of paraffin oil. The tube which serves to lead the CO₂ into the flask does not dip below the surface of the liquid. The contents of the flask are heated, while a stream of CO₂ passes through the whole apparatus, until the bubbles of gas rising in the Schiff's gas-measuring apparatus are sufficiently small to be negligible. After the air has thus all been removed a blank experiment of the phenylhydrazine hydrochloride solution is made before the actual determination is begun in order to allow for this error. For this blank experiment, 10 c.c. of the solution are accurately measured out with the requisite quantity of sodium acetate solution, diluted to 100 c.c. and 50 c.c. pipetted into the dropping funnel C; the end of this is drawn out into a hook-shaped capillary, and dips down to the bottom of the flask, the object being to prevent the collection of bubbles of gas; the stem of the funnel is first filled with water.

The solution in the funnel is allowed now to mix with



1. Instead of steam a current of carbon dioxide is used to drive the evolved nitrogen gas into the measuring tube.
2. Protection of the current of carbon dioxide from the absorptive action of the Fehling's solution by means of a thin layer of paraffin oil floating on the surface of the solution.
3. Absorption of the benzene in a suitable reagent.
4. Collection of the nitrogen in an ordinary Schiff's apparatus.

The reagents used are the following, and are the same as those used by Strache:—

Fehling's Solution.—CuSO₄ solution (70 grms. CuSO₄·5H₂O in 1 litre water). Alkaline potassium tartrate (350 grms. of tartrate and 260 grms. of KOH in 1 litre of water).

Sodium Acetate.—Ten per cent solution.

Phenylhydrazine Hydrochloride.—Five per cent solution.

* H. Strache, *Monatshefte für Chemie*, xii., 514; xiii., 252; Benedikt and Strache, *Ibid.*, xiv., 270; Hans Meyer, "Anleitung zur Quantitativen Bestimmung der organischen Atomgruppen."

the Fehling's solution, the funnel being then rinsed out once or twice with hot water. Any liquid tending to distil over while the mixture in the flask is being heated is condensed, and runs back into the flask by the inclined condenser D. The gas evolved by the reaction between the Fehling's solution and phenylhydrazine is now caught up in the current of CO₂, and carried into the absorption apparatus E, where it is washed free from benzene vapour; thence it is driven into the Schiff's apparatus filled with KOH solution (1:1). As soon as the bubbles have become as small again as before, the Schiff's apparatus is disconnected, allowed to stand some time, the gas volume being then read off, and reduced to 0° C. and 760 m.m. in the ordinary way.

The actual determination is made as soon as possible after the completion of this blank experiment.

Each determination requires about one hour for completion.

Of the substances suitable for absorbing the benzene vapour, the following were experimented upon:—

Paraffin oil and wax, caoutchouc, sulphuric acid, and a

mixture of sulphuric and nitric acids (nitrating mixture). Of these the nitrating mixture was found to act most suitably and to give the best results, especially when used in a bulb-absorption apparatus (see Fig.).

This mixture is made by mixing the acids in molecular proportions. The gas, after passing through the bulb-tube, is washed free from acid fumes by passing it afterwards through water contained in some suitable washing flask.

Determination of the Carbonyl Group in Hydroxybenzaldehyde.

Reagent used for absorption of benzene vapours.	CO per cent. Found.	CO per cent. Theory.
Sulphuric acid. . .	19.52	22.80
Paraffin oil . . .	23.64	
	23.83	
Nitrating mixture, $H_2SO_4 + HNO_3$. .	22.87	
	23.70	
	23.14	
	23.40	

Determination of the Carbonyl Group in Para-nitrobenzaldehyde.

Nitrating mixture . . .	19.22	18.53
	18.06	
	17.79	
	17.47	
	17.88	

Calculation of Results (Blank Experiment with Phenylhydrazine Solution).

Average of Results.—One c.c. of the solution evolved on oxidation with Fehling's solution 12.08 c.c. N at 760 m.m. and 0° C.

0.2686 grm. of the hydroxybenzaldehyde was mixed with 10 c.c. of the phenylhydrazine solution, and 15 c.c. of the sodium acetate solution added. After heating on the water-bath, the solution was made up to 100 c.c. with distilled water.

50 c.c. were used in the determination. 39.46 c.c. of nitrogen were evolved (measured and reduced to 0° C. and 760 m.m.).

$(5 \times 12.08) = 60.40$ c.c. = 39.46 c.c. = 20.94 c.c. of N, which represents the volume of nitrogen equivalent to the phenylhydrazine used in forming a hydrazone with the aldehyde. Then—

$$28.08 \text{ grms. N} = 28.00 \text{ CO} = 0.001256 : x.$$

$$x = 0.001252.$$

Or 1 c.c. of nitrogen is equivalent to 0.001252 grm. of CO; 20.94 c.c. are equivalent to 0.02622 grm. of CO; or the percentage—

$$\text{CO} = \frac{0.02622 \times 100}{0.1343} = 19.52 \text{ per cent of CO.}$$

My best thanks are due to Dr. F. Käuffer, of the Zürich Polytechnikum, for his kindly help and advice.

Zürich, January 28, 1906.

ANALYSIS OF ALLOYS OF COPPER.*

By JOHN M. WILSON,
Assistant Inspector of Engineering Material, U.S.N.

THE analysis of alloys of copper with other metals such as lead, tin, antimony, iron, aluminium, zinc, nickel, and phosphorus is not difficult, but requires time, patience, and a reasonable amount of care. It is not like the analysis of steel, in which the analyst may weigh out several suitable portions from which to separate a number of elements sought, as in the analysis of such alloys nearly all of the constituents must be obtained from a single quantity, and each, in its turn, must be separated completely from the solution before proceeding to the next. In some cases we may separate the elements into groups insoluble in certain reagents, after which we may work the several groups for the elements contained therein. In either instance care must be taken to insure complete separation and thorough washing, and where it is necessary solution and re-precipitation must be resorted to, in order to make the separation complete.

Before taking up the chemical portion of this question, I desire to emphasise the necessity of proper sampling of the materials under consideration. Alloys of copper and zinc, copper, zinc, and tin, and of lead and tin are particularly prone to separate into their constituent parts, especially when there is a difference in the specific gravity of these constituents, and for this reason great care must be used to obtain cuttings which represent all portions of the cast. This is easily accomplished, in sampling sheets, bars, and wire, by cutting the entire cross section, or boring entirely through the piece. In the case of complicated castings, however, it is not quite so easy of accomplishment.

The best method of obtaining cuttings for analysis is to clamp the piece in a shaping machine, setting the tool so that it cuts small granular pieces, the size of a pin's head. A milling tool in a drill press answers admirably, provided proper care is taken to insure absence of cuttings of any other material in the tool. An ordinary drill is not a good tool to use for this purpose, on account of the difficulty of properly regulating the pressure so as to obtain granular cuttings. Mr. Reddig, an Assistant Inspector of Hull Materials, U.S.N., stationed at Reading, has invented a drill which, as I understand it, is shaped much like a carpenter's bit, i.e., a gimlet point in the centre, from which, on one side, extends a nearly flat lip, and on the other a lip cut into saw-teeth, so that the drillings are powdered.

Considerable time may frequently be saved and a choice of method of analysis indicated, by making a qualitative analysis of the thoroughly mixed cuttings, noting the comparative proportions of lead, copper, tin, and the presence or absence of arsenic and antimony, as well as the presence or absence of manganese and phosphorus.

The removal of copper as metal and lead as peroxide simultaneously, from a nitric acid solution containing 5 per cent of its volume of concentrated acid, by the electric current expedites the analysis, and does away with the tedious and unsatisfactory washing of a precipitate of mixed sulphides of copper and lead. The former has a tendency to oxidise, with considerable rapidity, on exposure to the air, and dissolve in the wash, passing in solution through the filter, only to re-precipitate in the filtrate. This may be prevented to a large extent by keeping the filter full, until the washing is complete, before allowing it to drain.

Sulphide precipitates containing lead are best dead roasted in porcelain, then taken up in HNO_3 , and electrolysed. In the analysis of white metals the sulphide precipitate carries iron, and may contain zinc and nickel, in which case the liquid remaining after the removal of the lead and copper is to be neutralised with NH_4OH , and the

Royal Institution.—On Thursday next, March 1, at Five o'clock, Mr. Francis Darwin will deliver the first of three lectures at the Royal Institution on the "Physiology of Plants"; and on Saturday, March 3, at Three o'clock, Professor J. J. Thomson commences a course of six lectures on "The Corpuscular Theory of Matter." The Friday Evening Discourse on March 2 will be delivered by Dr. R. Caton, the subject being "Hippocrates and the Newly Discovered Health Temple at Cos"; and on March 9, by Dr. R. Hutchison on "Some Dietetic Problems."

* The Chemical Engineer, ii., No. 3.

Iron and other metals precipitated as sulphides, filtered off, and separated as described later.

The elements determined in these alloys are given below:—

Tin, in ordinary analyses, is that portion of the alloy insoluble in HNO_3 ignited over a blast-lamp.

Exact determination of tin is made by electrolysis of a solution in $\text{H}_2\text{C}_2\text{O}_4$ containing $(\text{NH}_4)_2\text{C}_2\text{O}_4$, after saturation with H_2S to remove antimony, and driving off the H_2S by heat. A current of 5 c.c. of electrolytic gas per minute is used, and allowed to run over night, when the tin will be found on the negative electrode as a grey coating. This may contain a little iron, which should of course be estimated and deducted.

Copper is deposited by the electric current from a HNO_3 solution containing about 5 per cent free acid by a current giving 5 c.c. of electrolytic gas per minute, and allowed to run over-night. The electrode is washed in the following manner:—The beaker is removed, and in its place is put one containing water, which is allowed to remain five to ten minutes; this, in turn, is removed, and a second beaker of water is raised and lowered sixteen times, in order to completely submerge the electrodes. This beaker is then removed, the current shut off, and the electrode disconnected, and placed in a beaker of alcohol, after which it is rinsed with ether, and dried over the steam table, being supported by its stem on a block of wood 2 inches square, and held down by a similar block.

Lead is separated at the same time as the copper, and deposited on the positive electrode as PbO_2 . The coating adheres well when the amount of lead is below 4 per cent and 1 grm. of material is used. When in excess of that amount, it flakes off, and can not be readily handled. When this occurs I usually make another determination, using half the quantity, and reversing the electrodes as recommended by Herrick.

Sometimes, however, the analysis is repeated, using 1 grm., and after removing the tin, the solution is evaporated with H_2SO_4 , diluted with water, the PbSO_4 filtered on a Gooch felt, ignited, and weighed. The filtrate is then electrolysed, and the lead not precipitated as sulphate obtained as PbO_2 . At other times the alloy is dissolved in $\text{HNO}_3 + \text{HCl}$, evaporated to a syrup, chilled by stirring, and the PbCl_2 precipitated by alcohol. The PbCl_2 is then taken up in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, and the lead precipitated and weighed as PbCrO_4 . Any lead not precipitated is found as PbO_2 on electrolysis of the copper.

I have frequently found that lead is not completely removed from solution as PbSO_4 , even by addition of alcohol. My attention was first called to this fact while making some analyses of babbitt metals. I found lead as PbSO_4 0.15 per cent upon electrolysing the filtrates for copper. I found as PbO_2 0.12 per cent. In white metals containing as high as 40 per cent lead, I invariably find 0.10 to 0.12 per cent lead as PbO_2 on electrolysing for copper.

Iron is determined by titration of its sulphate with KMnO_4 , 1 c.c. = 0.002 grm. Fe. Alloys which contain no tin are dissolved in HNO_3 , diluted to 300 c.c., the iron precipitated with NH_4OH , filtered, washed free from copper with NH_4OH and hot water, the $\text{Fe}_2(\text{OH})_6$ taken up in dilute H_2SO_4 , the solution reduced by passing through a zinc column, and titrated with KMnO_4 . Alloys containing tin are dissolved in $\text{HNO}_3 + \text{HCl}$, evaporated, the HNO_3 displaced with HCl , the solution made up to convenient volume, the copper, lead, tin, &c., precipitated and filtered through a dry filter, and a measured portion taken from which the iron is precipitated and estimated.

Aluminum is determined by difference.

Manganese in small amounts is weighed as Mn_3O_4 in large quantity as $\text{Mn}_2\text{P}_2\text{O}_7$.

Zinc in small amounts as ZnO by roasting ZnS , in amounts above 2 per cent as $\text{Zn}_3\text{P}_2\text{O}_7$. The solution is made neutral to methyl-orange, boiled, and $\text{NaNH}_4\text{HPO}_4$ solution added. The whole is then vigorously stirred and set aside at 80—90° C. until the flocculent precipitate

becomes granular and settles well, when it is filtered on a weighed Gooch felt, washed three or four times with hot water, dried at 100° C., ignited over a blast-lamp with cover on tight, cooled, and weighed.

This method of determining zinc is neat, expeditious, and exact; the precipitate filters rapidly, requires a minimum of washing, and is easily handled. A 10 per cent $\text{NaNH}_4\text{HPO}_4$ solution (neutral to methyl-orange) is employed as a precipitant, using 1 c.c. per 1 per cent Zn supposed to be present.

Phosphorus is precipitated by magnesia mixture from the $(\text{NH}_4)_2\text{S}$ solution of the insoluble in HNO_3 , and, after purification, weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

Nickel in small amount is weighed as NiO , in large amount by electrolysis or titration with KCN solution.

The electrolysis is made in a sulphate solution containing considerable $(\text{NH}_4)_2\text{SO}_4$ and a large excess of NH_4OH . A current of 10 c.c. electrolytic gas per minute is used for one and a-half hours, after which the current is increased to 15 c.c. per minute for another hour and a-half, at the end of which time the nickel should all be on the negative electrode.

Antimony is weighed as sulphide after ignition in a current of CO_2 .

Arsenic is not looked for quantitatively and seldom qualitatively in my laboratory, although it is used to a considerable extent in the manufacture of brass, to increase its tensile strength. Had I the time, therefore, I would test every sample received for this element. The best method is undoubtedly that of distillation after Lundin, as described by Blair, weighing the arsenic as As_2S_3 on a Gooch felt.

I will now describe briefly some apparatus and reagents used in the work.

Electrodes used are plain platinum cylinders, made without seams, to which are attached flattened wires well rivetted. The foil used is heavy, the better to stand wear and tear. The large cylinder is 2 inches high and 1½ inches in diameter and the small one is 2 by ½ inches.

Sodium Sulphide.—Being unable to obtain any sodium sulphide in the market suitable for the purpose, I prepare it, according to Classen, by dissolving one pound of caustic soda in five pints of water, dividing the solution into two approximately equal portions, one of which is saturated with H_2S (purified by passing through water and two U-tubes loosely packed with absorbent cotton) until it no longer increases in volume. The solution is then filtered into the other half, and the whole saturated as before, resulting in a light yellow solution, which is filtered into a large evaporating dish and evaporated rapidly till a pellicle forms, when the hot liquid is poured into 2 oz. bottles, the glass-stoppers sealed with paraffin, and the whole lot kept in a cool dark place. The solution keeps indefinitely without change of colour.

Ammonium Phosphate.—Add NH_4OH in slight excess to a 10 per cent solution of the salt, boil vigorously until nearly free from NH_3 , filter to remove any precipitate, and allow to cool. Make neutral to methyl-orange by the cautious addition of P_2O_5 or HCl .

Ammonium Sulphide is made in a similar manner to sodium sulphide, using two volumes water to one of concentrated NH_4OH , and omitting the evaporation.

Ammonium Acetate.— NH_4OH 400 c.c. + water 480 c.c. Add $\text{HC}_2\text{H}_3\text{O}_2$ glacial 340 c.c. The solution should be slightly acid to litmus; if not, add acid cautiously until the solution turns blue litmus red.

Solvent for White Metals.— HCl concentrated 800 c.c., HNO_3 concentrated 200 c.c., water 1000 c.c., KCl 4 grms.

Manganese Bronze.

Weigh 1 grm. into a No. 1 Griffin beaker, add 5 c.c. concentrated HNO_3 , heat on the steam table until no more nitrous fumes come off, add 25 c.c. water, digest until the insoluble matter, if any, appears perfectly white, filter through a double 7 c.m. ashless filter, and wash with 10 per cent HNO_3 until free from copper. Add NH_4OH

o the filtrate until a clear solution results, and then concentrated HNO_3 until the solution is acid and of a good copper-green colour, free from any yellow tinge. Add 5 c.c. HNO_3 in excess, and electrolyse over-night with a current of 5 c.c. electrolytic gas per minute. In the morning make sure the copper is all out of the solution, and if so, wash, dry, and weigh the electrodes for copper and $\text{PbO}_2 + \text{MnO}_2$. Dissolve the $\text{PbO}_2 + \text{MnO}_2$ from the electrode in hot HCl (1 to 1), evaporate to dryness, moisten with HNO_3 , evaporate until nearly dry, add 5 c.c. HNO_3 and 5 c.c. water, boil, and add PbO_2 . Boil two minutes longer, and allow to settle. If any violet colour of permanganic acid develops, titrate with standard sodium arsenite solution, and calculate the manganese so found to MnO_2 . Deduct from the weight of $\text{PbO}_2 + \text{MnO}_2$ found. The remainder will be PbO_2 . Calculate to Pb.

Although most writers claim that manganese is precipitated by electricity I have never found the amount precipitated together with the PbO_2 to exceed 0.05 per cent even in bronzes containing 3 to 34 per cent Mn.

Transfer the liquid remaining after removal of copper and lead, together with the washings, to a No. 4 beaker, boil, precipitate the iron and alumina with NH_4OH , filter into a large flask, reserve filtrate, dissolve precipitate in HCl , and precipitate with NH_4OH . Repeat once more to insure complete separation of Mn + Zn from Fe and Al.

Unite the three filtrates, make nearly neutral, and add enough bromine to colour the solution. Pour down the sides of the flask, in order to mix as little as possible, 75–100 c.c. NH_4OH , and allow to stand in the cold until the bromine has nearly disappeared from the bottom of the flask. Warm the flask gently, and bring its contents to a boil. Continue boiling until the precipitated MnO_2 collects in flasks, allow to settle, filter through paper. Wash three times with hot water, reserve filtrate, dissolve precipitate in $\text{HCl} + \text{H}_2\text{SO}_3$, boil off SO_2 , make slightly ammoniacal, and re-precipitate the manganese as before.

Unite the filtrates, evaporate to about 400 c.c., cool, make just neutral to methyl-orange, boil, and add $\text{NaNH}_2\text{HPO}_4$ (1 c.c. per each 1 per cent Zn calculated). Stir, set in a warm place (80 to 90° C.) until the precipitate becomes granular and settles well, filter through weighed Gooch felt, wash three or four times with hot water, dry at 100° C., ignite over a blast, with cover on tight, cool, and weigh as $\text{Zn}_2\text{P}_2\text{O}_7$.

Weigh 5 grms. into a No. 4 beaker, add 5 c.c. concentrated HNO_3 + 25 c.c. concentrated HCl , evaporate to dryness on a steam-plate, moisten with HCl , and evaporate again. Add 20 c.c. HCl + 50 c.c. water, boil, filter into 500 c.c. graduated flask, wash twice alternately with hot HCl (1–1) and cold water, then several times with hot water, ignite, and weigh the residue. Test SiO_2 with $\text{HF} + \text{HNO}_3$.

Calculate to Si, which is usually about 0.03 per cent. Make filtrate up to mark, pour into a beaker, warm to 60 to 80° C., saturate with H_2S , and filter through a dry ribbed filter into a 500 c.c. graduate until 400 c.c. have run through. Reject the filter and precipitate, transfer the filtrate to a beaker, evaporate to small volume or to dryness, and oxidise with HNO_3 , and boiling. The volume should now be 100 to 150 c.c. Make three basic acetate separations, precipitate, ignite, and weigh as Mn_3O_4 . If large take up in $\text{HCl} + \text{H}_2\text{SO}_3$, NH_4OH , and, if the precipitate is small, wash well with hot water, ignite, and weigh as Mn_3O_4 . If large take up in $\text{HCl} + \text{H}_2\text{SO}_3$, evaporate to dryness, moisten with HCl , take up in hot water, add 10–20 c.c. $\text{NaNH}_2\text{HPO}_4$, boil, add NH_4OH until a precipitate forms, stir till this becomes silky, and then add NH_4OH , a drop at a time, stirring constantly until the liquid smells distinctly of NH_3 . Set aside two to three hours, filter on a weighed Gooch felt, wash with NH_4OH (1 to 3) containing NH_4NO_3 , dry on the steam-table, ignite, and weigh as $\text{Mn}_2\text{P}_2\text{O}_7$. Calculate to manganese.

Dissolve the iron and alumina precipitate in dilute HNO_3 , precipitate with NH_4OH in a volume of 350 c.c., and filter. Wash twice on the filter (it is not necessary to

wash much, as any NH_4NO_3 adhering to the precipitate assists in preventing reduction of Fe_2O_3 during ignition), and transfer precipitate and wet filter to a platinum crucible. Moisten the filter thoroughly with concentrated HNO_3 , dry on a steam-table, place over a Bunsen turned low, with the crucible cover on nearly tight, and raise the temperature slowly to the full heat of the Bunsen. Roast one hour, ignite over blast fifteen minutes, raising cover occasionally, and weigh before crucible is cold. Repeat ignition, and weighing until the weight is constant. The precipitate is $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$.

Fuse precipitate with eight to ten times its weight of $\text{K}_2\text{S}_2\text{O}_7$ for several hours at a temperature just sufficient to drive off a little SO_3 . Leach melt in water, and filter off, estimate and deduct a little SiO_2 . Reduce the filtrate and titrate the iron. Calculate to Fe_2O_3 and also to iron ($\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$) – $\text{FeO}_3 = \text{Al}_2\text{O}_3$. Calculate to aluminum.

(To be continued).

CONDENSATION COMPOUNDS OF CAMPHOROXALIC ACID AND AMINES.*

SEVENTH COMMUNICATION ON CAMPHOROXALIC DERIVATIVES.†

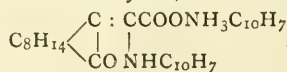
By J. BISHOP TINGLE, Ph.D., F.C.S.,
and
WILLIAM EDWIN HOFFMAN, Jun., Ph.D.
(Continued from p. 74).

ACTION OF AMINES ON CAMPHOROXALIC ACID.

I. β -Naphthylamine.

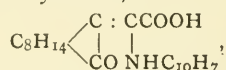
β -NAPHTHYLAMINE and camphoroxalic acid yield three compounds:—

1. The first of these, β -naphthylamine- β -naphthylcamphoformeneaminocarboxylate,—



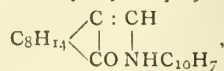
is formed in hot alcoholic solution and crystallises in slender pale yellow needles, melting at 166°.

2. The second compound is obtained when this salt, in very dilute alcoholic solution, is treated with sodium hydroxide and the product acidified. β -Naphthylcamphoformeneaminocarboxylic acid,—



crystallises from alcohol in slender bright yellow needles, melting at 172.5°. This compound has been previously described by J. Bishop Tingle and Alfred Tingle (*Journ. Am. Chem. Soc.*, 1901, xxiii., 375).

3. The third compound from β -naphthylamine and camphoroxalic acid, β -naphthylcamphoformeneamine,—

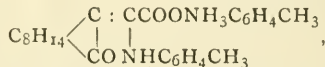


is formed by heating either of the preceding substances above its melting-point. It crystallises in slender pale yellow prisms, melting at 173°.

II. Paratoluidine.

Paratoluidine and camphoroxalic acid yield a series of three compounds, corresponding to those formed by β -naphthylamine.

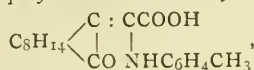
1. The p-toluidine p-tolylcamphoformeneaminocarboxylate,—



* From the *American Chemical Journal*, xxxiv., No. 3.

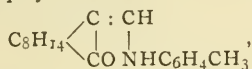
is formed in alcoholic solution, and crystallises readily from alcohol in pale yellow needles, melting at 152°.

2. *p*-Tolylcamphorformeneaminecarboxylic acid,—



is formed from the above salt by treatment with sodium hydroxide solution and subsequent acidification of the product. It crystallises from benzene in pale yellow prisms melting at 168°.

3. *p*-Tolylcamphorformeneamine,—

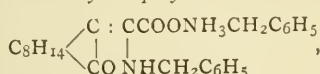


is formed by heating either of the two preceding substances above its melting-point. From alcohol it crystallises in slender yellow prisms melting at 178°.

III. Benzylamine.

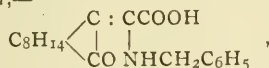
Benzylamine forms with camphoroxalic acid a series of three compounds, similar to those produced by β -naphthylamine and *p*-toluidine.

1. Benzylamine benzylcamphorformeneaminecarboxylate,—



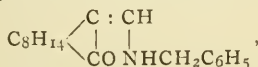
is obtained by the action of the free base on camphoroxalic acid, and crystallises from alcohol in irregular rhombohedra melting at 174.5°.

2. From the above salt, free benzylcamphorformeneaminecarboxylic acid,—



is formed by treating it with sodium hydroxide and acidifying the resulting solution. It is a colourless compound, crystallising from ethyl acetate in clusters of fine prisms, melting at 140°.

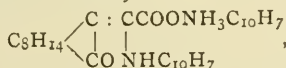
3. When heated above its melting-point, each of the preceding compounds decomposes, forming benzylcamphorformeneamine,—



which from alcohol crystallises in colourless prisms melting at 96.5°.

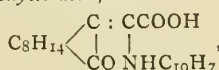
IV. α -Naphthylamine.

From α -naphthylamine and camphoroxalic acid two compounds are obtained; α -naphthylamine naphthylcamphorformeneaminecarboxylate,—



is formed in alcoholic solution, and, when purified by means of this solvent, yields greenish yellow prisms melting at 165°.

2. The above salt, when heated with sodium hydroxide solution and the product acidified, gives α -naphthylcamphorformeneaminecarboxylic acid,—



which crystallises from benzene with 0.5 molecule of benzene and melts at 170°.

This acid has been described by J. Bishop Tingle and Alfred Tingle (*Journ. Am. Chem. Soc.*, 1901, xxiii., 375).

3. When heated above its melting-point, each of the two preceding substances formed a viscous mass, from which no definite compound could be isolated.

V. Metatoluidine.

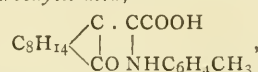
Metatoluidine and camphoroxalic acid also yield two compounds:—

1. Metatoluidine metatolylcamphorformeneaminecarboxylate,—



is formed when the free acid and amine react in alcoholic solution; it crystallises from alcohol in fine pale lemon coloured needles melting at 126°.

2. The above salt, when treated with sodium hydroxide solution and the product acidified, gives metatolylcamphorformeneaminecarboxylic acid,—

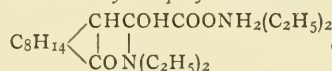


which crystallises from benzene in colourless needles and melts at 154°. When heated above its melting-point, each of the preceding substances formed a viscous mass, from which no definite compound could be isolated.

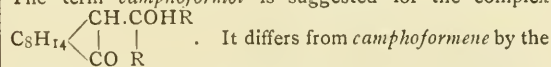
VI. Diethylamine.

Diethylamine and camphoroxalic acid react in alcoholic solution to form two compounds:—

1. Diethylamine diethylcamphorformolaminecarboxylate,—

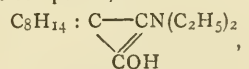


This compound crystallises from alcohol in colourless needles melting at 139.5°. It differs from the foregoing salts of camphorformeneaminecarboxylic acid in that its formation does not involve the elimination of the elements of water, in which respect it resembles the hydroxylamine derivative previously referred to (p. 72). With an alcoholic solution of ferric chloride no colour reaction is produced. The term *camphoformol* is suggested for the complex

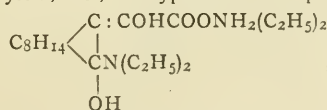


It differs from *camphoformene* by the addition of the elements of water, one hydrogen atom being united to the camphor nucleus.

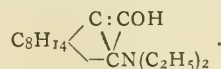
2. When this salt is heated above its melting-point it gives off water, carbonic anhydride, and diethylamine, and forms a compound of the same empirical formula as diethylcamphorformeneamine, $\text{C}_{15}\text{H}_{25}\text{NO}$, but which differs from what we should expect of that substance by virtue of the fact that, with ferric chloride and alcohol, it gives the reddish violet colour characteristic of the enol grouping; this seems to indicate that the reaction leading to its formation is hardly so simple as that which yields the corresponding derivatives of other amines. It may be possible that an isomeric compound,—



is produced, or it may be that diethylamine and camphoroxalic acid yield, first, the hypothetical compound,—



which, when heated, would doubtless give a body with the formula—

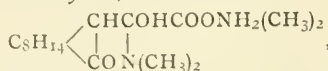


This matter will be investigated at the first suitable opportunity, because the substance in question might furnish an interesting case of dynamic isomerism.

The compound crystallises from ethyl acetate in colourless needles melting at 153°.

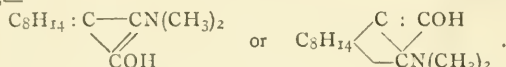
VII. Dimethylamine.

1. Dimethylamine and camphoroxalic acid in alcoholic solution react to form *dimethylamine dimethylcamphorolaminocarboxylate*,—



which crystallises from acetone in colourless needles melting at 137.5°. Like the corresponding compound from diethylamine, it is apparently formed by the direct combination of acid and base, without the loss of a molecule of water.

2. When the salt which has just been described is heated above the melting-point, it decomposes similarly to the analogous diethyl compound and forms a substance of the same empirical formula as dimethylcamphorformeneamine, $\text{C}_{13}\text{H}_{21}\text{NO}$, but which, on account of the fact that it gives a colour reaction with ferric chloride, does not seem to have that structure. It appears probable that its constitution is similar to that of the diethyl derivative, and that its formula is—



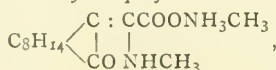
It crystallises from alcohol in colourless needles melting at 63°.

It is worthy of note that dimethylamine and diethylamine are the only two secondary amines from which it has been possible to obtain derivatives with camphoroxalic acid. Methylaniline and ethylaniline entirely fail to give definite compounds under similar conditions; whether this is due to the general tendency of these two substances to yield oily salts, or to their feeble basic properties as compared with the aliphatic amines, or to some other cause, must at present remain uncertain.

VIII. Methylamine.

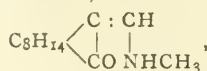
Methylamine forms two compounds with camphoroxalic acid:—

1. *Methylamine methylcamphorformeneaminocarboxylate*,—



which crystallises from alcohol in slender colourless needles melting at 172°.

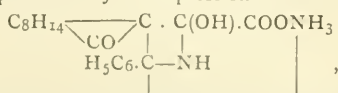
When this salt is heated above its melting-point, it forms *methylcamphorformeneamine*,—



which crystallises from ethyl acetate in colourless needles melting at 131°.

IX. Benzamidine.

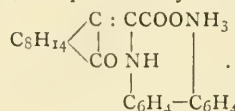
Camphoroxalic acid in alcoholic solution reacts with benzamidine in equimolecular proportion to form a colourless crystalline compound melting at 184°. At a slightly higher temperature it decomposes to a carbonaceous mass. Dilute acids and solutions of alkalis seem to have no effect upon the compound and ferric chloride in alcoholic solution does not give any colour reaction. The substance has the empirical formula $\text{C}_{19}\text{H}_{24}\text{O}_4\text{N}_2$. Its constitution may perhaps be represented by the expression—



but further work will be necessary to decide this point.

X. Benzidine.

Benzidine reacts with camphoroxalic acid in hot alcoholic solution, eliminating water and forming a greenish-yellow crystalline mass, which melts at 190° and decomposes when maintained at this temperature or heated for a short time at a higher one. The compound is apparently unchanged by the action of acids or alkalis and does not give any colouration with ferric chloride in alcoholic solution. In view of these facts and of the properties of benzidine itself, it is probable that one of the amino-groups has combined with the :COH group with the elimination of water, while the other has reacted with the carboxyl hydrogen to form a salt, as represented by the formula—



(To be continued).

PERKIN MEMORIAL AND JUBILEE OF THE COAL-TAR COLOUR INDUSTRY.

PUBLIC MEETING AT THE MANSION HOUSE.

THE year 1906 marks the fiftieth anniversary of the epoch-making discovery by William Henry Perkin of the dye-stuff "Mauve," by which the foundation was laid of the Coal Tar Colour Industry, and a great stimulus given to the study of organic chemistry.

The discoverer, Dr. Perkin, being fortunately still with us in full activity, it has been widely felt in this country and abroad that the jubilee of the foundation of this important industry should be made the occasion of a fitting public tribute to its founder, in recognition of the great services he has rendered to chemical industry and chemical science by his life work. We are also assured that the movement if inaugurated here would meet with the warmest support in Germany, where the seed first sown by Perkin has grown into an industry of national importance worth many millions a year. Those connected with this industry in Germany, we are led to believe, would welcome the opportunity of according to its founder some mark of appreciation and gratitude. It is also probable that in other countries we may count upon a generous measure of support.

With the object of considering what steps should be taken to give effect to the suggested memorial and jubilee celebration, a public meeting will be held at the Mansion House, London, on Monday, February 26th, at 3 p.m., at which the Lord Mayor has kindly consented to preside.

The meeting will be asked to recommend the opening of a subscription list for effecting the following objects:—

1. The presentation to Dr. Perkin for his lifetime of an oil portrait of himself, executed by an eminent artist, the portrait to become the property of the nation at his death.
2. The execution of a marble bust of Dr. Perkin to be placed in the rooms of the Chemical Society.
3. The establishment of a "Perkin Research Fund" for the promotion of chemical research, to be administered through the Chemical Society.

A strongly representative Provisional Committee of supporters of the scheme has been formed under the chairmanship of Prof. R. MELDOLA, F.R.S., President of the Chemical Society, which includes many important public men, scientists, and manufacturers.

Acyclic 8-Chlorethyl and Vinyl Ketones.—E. E. Blaise and M. Maire.—The vinyl ketones can be prepared without much difficulty, and with satisfactory yields from the 8-chlorethyl ketones. It is only necessary to boil the latter with diethylaniline under suitable conditions, $\text{CH}_2\text{Cl}-\text{CH}_2-\text{CO}-\text{R} \rightarrow \text{CH}_2=\text{CH}-\text{CO}-\text{R}$.—*Comptes Rendus*, cxlii., No. 4.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 1st, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

Concluded from p. 78.

*23. "The Relation between Absorption Spectra and Chemical Constitution. Part II. The Quinones and α -Diketones." By EDWARD CHARLES CYRIL BALY and ALFRED WALTER STEWART.

In the preceding communication, it was shown that in the absorption spectrum of ethylpyruvate an absorption band is developed in a different region and at a different dilution from the bands given by the substances having a labile hydrogen atom (Baly and Desch, *Trans.*, 1904, lxxxv., 1029; 1905, lxxxvii., 766). This band was shown to be due to the two carbonyl groups in juxtaposition to one another; when two such carbonyl groups are present in the molecule, a new type of oscillation is induced, resulting in the absorption of light of a much longer wave-length than is absorbed by the process of enol-ketotautomerism. For this new type of oscillation, the name isorropesis was proposed. In the present paper it was shown that this isorropesis in α -diketones results in the absorption of light in the visible blue region, so that the substances are intensely yellow. This is evidenced by camphorquinone and diacetyl. An analogous condition in the close proximity of the carbonyl groups occurs in benzoquinone. It is shown that quinone develops the same absorption band as do diacetyl and camphorquinone. The process of isorropesis occurs therefore in benzoquinone exactly as in the case of the α -diketones, and is the origin of the yellow colour of this substance. The same is found to be true in the case of β -xyloquinone, toluquinone, α -naphthaquinone, acenaphthenequinone, and phenanthraquinone. There is little doubt, therefore, that the yellow colour of the quinones is due to the isorropesis between the carbonyl groups in juxtaposition. These observations strongly support Armstrong's theory that the colour of certain benzene derivatives is due to the quinonoid linking, for they show that the colour is caused, not directly by this linking, but by the isorropesis between the unsaturated atoms where this linking exists.

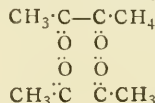
*24. "The Relation between Absorption Spectra and Chemical Constitution. Part III. The Nitranilines and the Nitrophenols." By EDWARD CHARLES CYRIL BALY, WALTER HENRY EDWARDS, and ALFRED WALTER STEWART.

In this paper are described the absorption spectra of compounds having the quinonoid linking and containing a nitrogen atom in place of one or both of the quinone oxygen atoms. By a comparison of the absorption spectra of the nitranilines with those of their hydrochlorides, it is shown that the free substances must exist in the quinonoid form, and that, as they show the same absorption band as benzoquinone and the α -diketones, a similar process of isorropesis takes place between the unsaturated nitrogen atoms as between the oxygen atoms of benzoquinone and the α -diketones. Similar arguments are found to hold good for the nitrophenols and for nitrosophenol. By these observations the principle developed in the preceding papers, that the colour of the quinones is due to the oscillation or isorropesis between the oxygen atoms, is extended to those quinonoid compounds containing nitrogen atoms in the place of one or both of the oxygen atoms.

DISCUSSION.

Prof. ARMSTRONG said that Mr. Baly had put aside entirely the view which had long been held that ketonic interactions were conditioned by the combination of various substances with the carbonyl group, and had adopted an entirely *intra*-molecular view of change, whether chemical or physical. He, however, was inclined

to advocate the view that the changes were *inter*-molecular. He also still adhered to the opinion that three absorbing centres were required to produce visible colour, *i.e.*, that iodoform, not methylene iodide, might be taken as typical of coloured substances. From this point of view, the colour of compounds such as diacetyl might be accounted for on the assumption that polymeric molecules were present, formed by the association, through the residual affinity of the oxygen atoms, of the ketonic groups, *e.g.* :—



This explanation might perhaps apply also to metanitrophenol and metanitraniline. He remarked subsequently that the blue colour of water might be accounted for from this point of view, but not by Mr. Baly's hypothesis.

In reply to Prof. Armstrong, Mr. BALY pointed out that the absorption spectrum of acetone and ethyl acetoacetate in aqueous solution shows that the tautomeric process is much decreased by the action of the solvent. Similarly, in the case of benzoquinone, the absorption band due to isorropesis exhibited in alcoholic solution entirely disappears when the substance is examined in aqueous solution, its place being taken by two bands in the ultra-violet region. These facts, due no doubt to the formation of hydrates, are strong evidence against the suggestion made by Prof. Armstrong, that the colour of diacetyl is due to a complex of two molecules of this substance.

*25. "The Action of Light on Benzaldehydephenylhydrazone." By FREDERICK DANIEL CHATTAWAY.

Fischer, who first prepared the ordinary stable α -modification of benzaldehydephenylhydrazone (*Annalen*, 1878, cxc., 135), noted that it reddened when exposed to the air, and this observation was confirmed by Biltz (*Zeit. Physikal. Chem.*, 1899, xxx., 527), and Reutt and Pawlewski (*Bull. Acad. Sci. Cracow*, 1903, 503), who added that the reddening takes place on exposure to light, and disappears when the compound is heated or placed in the dark. The author has extended these observations, and shows that the presence or absence of air does not affect the coloration which is brought about by the violet and blue portions of the spectrum only. The changes of colour are probably due to a reversible isomeric change from the hydrazino- to the azo-configuration,—



The colour produced in benzaldehydephenylhydrazone when it has reached its maximum exactly equals in shade and intensity that of azobenzene itself. This explanation of the colour change is supported by the behaviour of benzaldehydediphenylhydrazone and benzaldehydebenzylphenylhydrazone, which are not capable of undergoing this type of change, and which are not altered in colour by light.

This intramolecular rearrangement caused by light and accompanied by colour change leads to the suggestion that the fading of organic colouring matters in sunlight may in some cases at least be due to a similar reversible isomeric change.

DISCUSSION.

Dr. WADE, who asked whether the author had noticed the production of the coloured modification of the hydrazone at the moment of its formation, more especially in benzene solution, stated that he had experienced great difficulty in obtaining a colourless product when the reacting substances were dissolved in this solvent.

Mr. W. ROBERTSON pointed out that according to the Hantzsch-Werner hypothesis two stereoisomerides are possible; in the case, however, of the benzaldehydephenylhydrazones, three isomeric modifications are known, and it is highly probable that all three possess different constitutions. The significance of the colour of the substituted benzaldehydephenylhydrazones when taken in con-

junction with the red unstable "benzylidenephnylhydrazine," was explained and the opinion expressed that the nitrobenzaldehydephenylhydrazones were, in reality, stable azo-compounds.

26. "The Union of Chlorine and Hydrogen." By CHARLES HUTCHENS BURGESS and DAVID LEONARD CHAPMAN.

The authors have investigated the dependence of the character of the induction period on the conditions. The results obtained increased the difficulty of explaining the phenomenon in question by the theory of an intermediate compound. They also indicated that the effect must be due to some retarding impurity. The impurity was found to be a gaseous compound resulting from the interaction of chlorine and ammonia. An inhibitive compound can also be formed by the action of chlorine on compounds capable of yielding ammonia on oxidation. When such substances are present in the actinometer, the retarding impurity can be gradually formed for considerable periods of time, so that the mixture after it has been previously induced can again become inert when it is allowed to remain in the dark. If the gases and the water contained in the actinometer are carefully purified from all ammoniacal impurity, no induction period can be observed even after the actinometer has stood for weeks in the dark.

Ammonia (chlorine-substituted ammonia) retards the action between chlorine and formaldehyde in the light. Its inhibitive effect is, however, much less in this case.

No difference could be detected in the absorption coefficients of mixtures in equal volumes of air and chlorine and of hydrogen and chlorine. The energy which brings about the combination of hydrogen and chlorine is therefore probably derived from the light absorbed by the chlorine in virtue of its optical properties.

27. "Note on the Molecular Weight of Epinephrine." By GEORGE BARGER and ARTHUR JAMES EWINS.

Abel and Taveau have recently (*Journ. Biol. Chem.* 1905, i., 1) objected to the formula $C_9H_{13}O_3N = 183$ for epinephrine (adrenaline), the active principle of the adrenal gland. They prefer the formula $2(C_{10}H_{13}O_3N, 4H_2O) = 408$, and criticise the molecular weight determinations of previous investigators, arguing that the use of acetic acid is "entirely inadmissible," since the substance cannot be recovered unchanged from the solution. Von Firth (*Monatsh.*, 1903, xxiv., 261) has shown that at least part of the substance can be obtained crystalline by ammonia after evaporating the acetic acid in a vacuum, and the authors have confirmed this observation.

That the loss of epinephrine is extremely small in acetic acid solution was shown by Dr. H. H. Dale, who, using a physiological method indicated by Elliott (*Journ. Physiol.* 1905, xxxii., 447), finds it possible to estimate epinephrine with an accuracy of about 5 per cent. This physiological method also served as a criterion for the purity of the epinephrine employed, the most active specimen obtained by repeated fractional precipitation with sodium carbonate and ammonia being selected.

The microscopic method of molecular weight determination (*Trans.*, 1905, lxxxvii., 1756) was employed, with glacial acetic acid and with benzaldehyde, at a temperature of 90°.

I. 0.0732 grm. in 2.00 grms. of acetic acid was intermediate between 0.19 and 0.214 grm.-molecule of benzil per 1000 grms. of solvent. $M = 172-193$.

II. 0.1016 grm. in 2.00 grms. of acetic acid was intermediate between 0.166 and 0.18 grm.-molecule of acetanilide per 1000 grms. of solvent. $M = 180-194$.

III. 0.0732 grm. in 2.00 grms. of acetic acid was intermediate between 0.205 and 0.21 grm.-molecule of benzil per 1000 grms. of solvent. $M = 174-179$.

IV. 0.0732 grm. in 2.00 grms. of benzaldehyde was intermediate between 0.21 and 0.22 grm.-molecule of benzil per 1000 grms. of solvent. $M = 167-174$.

The mean of all these values is 179.

The epinephrine solutions in Experiments II. and III. were heated to 90° for ten minutes (the time during which the capillary tubes were heated), then diluted with water, nearly neutralised, and made up to 1 in 10,000. On comparison with a solution of the same strength, made by dissolving the solid epinephrine in the minimum quantity of hydrochloric acid, Dr. Dale could not trace any loss of physiological activity.

The value obtained by Jowett (*Trans.*, 1904, lxxxv., 194) in a very dilute glacial acetic acid solution by the freezing-point method was 135, and by Bertrand (*Comptes Rendus*, 1904, cxxxix., 502) was 174.3. It would appear, therefore, that Abel's formula should be abandoned.

28. "The Critical Temperature and Value of ML/Θ of some Carbon Compounds." By JAMES CAMPBELL BROWN.

The critical temperatures of a number of organic alcohols, acids, esters, and aromatic hydrocarbons are determined. The latent heats of the re-purified substances have been re-determined, and the values of the constant ML/Θ are calculated for a number of these compounds for which this constant could not be given (*Trans.*, 1903, lxxxiii., 987, and *Trans.*, 1905, lxxxvii., 265). Two or three of the boiling-points are given more correctly for the purified substances.

The value of ML/Θ rises very slightly with the increase of CH_2 in the aliphatic alcohols, acids and esters, but is very constant for the aromatic hydrocarbons.

(NOTE.— ML = molecular heat of vapourisation, Θ = absolute temperature of the boiling-point).

29. "Slow Oxidations in the presence of Moisture." By NORMAN SMITH.

Experiments have been carried out to determine whether the oxidation of ammonia at the ordinary temperature in the presence of air and water could be brought about (1) by catalysis, (2) by induced oxidation. The catalysts used were ferric oxide, stannic oxide, manganese dioxide, lead peroxide, and platinum. Stannic oxide and manganese dioxide produced both nitrite and nitrate from the ammonia (0.05 m.grm. of nitrate for 5 grms. of oxide used); ferric oxide and lead peroxide gave only small amounts of nitrite and nitrate (0.01 m.grm. of nitrate), whilst platinum appeared to be without action. With platinum heated to a temperature just below dull redness, however, a very dilute solution of ammonia or ammonium salts was readily oxidised in presence of air. In the presence of copper or tin undergoing oxidation in air, ammonia was readily oxidised to nitrite and nitrate; zinc in some experiments gave positive, and in others negative results, whilst ferrous and manganous hydroxides showed only traces of nitrite or nitrate. In the cases where the formation of nitrate was brought about by induced oxidation, the amount of nitrate produced was much greater than with catalysts.

The experiments were extended to the case of nitrogen. No evidence of oxidation of nitrogen by catalysts was obtained. In the presence of substances undergoing oxidation, the metals, zinc, iron, and magnesium only among a large number of substances investigated gave ammonia, nitrite, or nitrate. These results were shown to be probably due to traces of nitride in the metals.

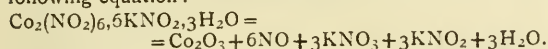
Water was evaporated in air, under various conditions, and it was shown that in no case was ammonium nitrite produced (compare Schönhein, *Journ. Prakt. Chem.*, 1861, lxxxiv., 215, and others) if the following sources of error were avoided:—(a) Traces of nitrite in the air, (b) nitrites produced in the burning of flames, (c) presence of ammonium compounds or albuminoid matter in the water, (d) traces of nitride in the metals.

No hydrogen peroxide was produced in the evaporation of water under various conditions, except in presence of certain metals such as zinc, which undergo rapid oxidation at the same time.

30. "Fischer's Salt and its Decomposition by Heat." By PRAFULLA CHANDRA RAY.

Fischer's salt as ordinarily prepared seems to correspond to the formula $Co_2(NO_2)_6, 6KNO_2, 3H_2O$. It is, however, invariably contaminated with appreciable traces of an oxide

of cobalt. The method of Rosenheim and Koppel evidently does not yield a purer product as claimed by them. The salt when heated in a vacuum decomposes according to the following equation:—

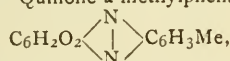


On this decomposition is based an accurate and expeditious method of analysing the compound.

31. "Action of Quinones on o-Diamines, o-Nitroaniline, m-Nitroaniline, and 2-Nitro-p-toluidine." (A Preliminary Note). By JAMES LEICESTER.

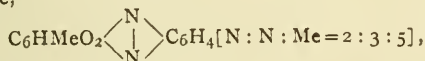
In a previous paper (*Ber.*, 1890, xxiii., 2793; *Abstr.*, 1890, 1445), it was shown that the action of o-nitroaniline and 2-nitro-p-toluidine on benzoquinone, toluquinone, and naphthaquinone was the same in principle as that occurring in the case of aniline and benzoquinone. Quinone-fluorindines and quinonephenazine derivatives were obtained on reduction with ammonium sulphide (*Proc.*, 1893, ix., 9).

Homofluorindine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{N} \\ \diagdown \quad \diagup \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, has now been prepared from quinonehomofluorindine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{O}_2 \begin{smallmatrix} \text{N} \\ \diagdown \quad \diagup \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, by reduction with hydriodic acid (O. Fischer and E. Hepp, *Ber.*, 1890, xxxiii., 2789, and *Ber.*, 1888, xxi., 683). Various salts of the base have been made. Quinone- α -methylphenazine,—

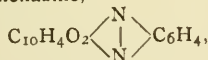


has also been reduced in a similar way. Some of the salts dissolve in alcohol with a deep blue colour, and have a red fluorescence; the slightest trace of ammonia changes the colour to bright red with a strong fluorescence.

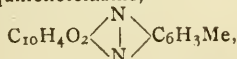
The absorption spectra of some of the compounds are under investigation with a view to the question of the origin of colour in organic compounds. Quinonephenotolazine,—



naphthaquinonephenazine,—



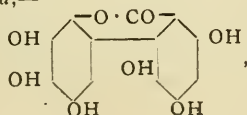
and α -naphthaquinonetolazine,—



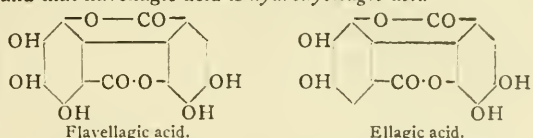
are also being examined in a similar manner.

32. "Some Oxidation Products of the Hydroxybenzoic Acids." (II.). By ARTHUR GEORGE PERKIN.

When gallic acid dissolved in 76 per cent sulphuric acid is oxidised by means of potassium persulphate, a colouring matter very similar to ellagic acid is produced. This substance, $\text{C}_{14}\text{H}_6\text{O}_9$, to which the name *flavellagic acid* is assigned, is obtained in yellow needles (m. p. above 360°), and dissolves in alkalis with a greenish yellow coloration, and gives an acetyl compound, $\text{C}_{14}\text{H}_6\text{O}_9(\text{C}_2\text{H}_5\text{O})_5$ (colourless needles, m. p. $317-319^\circ$), and a benzoyl derivative, $\text{C}_{14}\text{H}_6\text{O}_9(\text{C}_7\text{H}_5\text{O})_5$ (prismatic needles, m. p. $287-289^\circ$). On distillation with zinc dust, it gives *fluorene*, and on digestion with boiling potassium hydroxide solution is converted into a substance, $\text{C}_{13}\text{H}_8\text{O}_8$ (m. p. above 360°), the alkaline solution of which develops a bluish violet colour on oxidation. It crystallises with $1\text{H}_2\text{O}$ in almost colourless needles, gives an acetyl compound, $\text{C}_{13}\text{H}_8\text{O}_8(\text{C}_2\text{H}_5\text{O})_6$ (prismatic needles, m. p. $232-234^\circ$), and a corresponding benzoyl derivative (m. p. $261-263^\circ$). The results indicate that this substance is *hexahydroxydiphenylmethyliodide*,—



and that flavellagic acid is *hydroxyellagic acid*—



When gallic acid is oxidised in acetic acid by means of potassium persulphate and sulphuric acid, *ellagic acid* is formed, and this process is preferable to that in which concentrated sulphuric acid is employed as the solvent (*Proc.*, 1905, xxi., 185), owing to the simultaneous production in this case of a small quantity of flavellagic acid. These colouring matters could only be separated in the form of their benzoyl derivatives.

33. "Contributions to the Chemistry of Oxygen Compounds. Part I. The Compounds of Tertiary Phosphine Oxides with Acids and Salts." By ROBERT HOWSON PICKARD and JOSEPH KENYON.

Tertiary phosphine oxides are easily prepared by the action of phosphorus oxychloride on organo-magnesium compounds. They combine with acids, metallic salts, and organo-magnesium iodides, forming compounds having the general formulæ $(\text{R}_3\text{PO})_2, \text{H}_n\text{X}$, $(\text{R}_3\text{PO})_2, \text{M}''\text{X}_2$, and $(\text{R}_3\text{PO})_2, \text{CH}_3\text{MgI}$. The compounds described include some of those in which R is methyl, ethyl, propyl, phenyl, or benzyl, HX is ferrocyanic, chlorauric, cobaltcyanic, dichromic, camphoric, iodobismuthic, or iodomercuric acids, and $\text{M}''\text{X}_2$ is zinc chloride or iodide, cadmium iodide, mercuric or cobalt chlorides. Other compounds of the oxides which do not conform to these general formulæ are those with hydrochloric, trichloroacetic, pyruvic, and chloroplatinic acids and cupric chlorides. The constitution of these compounds is best explained by Werner's theory of oxonium compounds (*Annalen*, 1902, cccxxxiii., 296). The oxides are very weak bases. Their aqueous solutions do not affect the birotation of dextrose, and their compounds with acids are hydrolysed to a large extent by water.

34. "The Rapid Electro-analysis of Metals." (Preliminary Note). By HENRY JULIUS SALOMON SAND.

A method for the rapid electro-deposition of metals for analysis and their separation by graded potential has been elaborated. Silver has thus been accurately separated from copper in about six minutes from boiling acetate solutions, more than half a grm. being deposited without the use of an auxiliary electrode. Copper was separated from bismuth from a boiling tartrate solution (time, about eight minutes). An auxiliary electrode is necessary. The operation must be repeated once, as the first deposit contains traces of bismuth. Owing to the high stirring-efficiency of the electrodes, bismuth has been easily obtained in a perfectly adherent form from nitrate solutions, the time required being about ten minutes, with no auxiliary electrode. By treating the precipitation of bismuth as a separation from hydrogen, perfectly adherent metallic deposits have also been obtained from tartrate and acetate solutions (with the use of an auxiliary electrode). So far the deposition of the following metals has been studied and successfully carried out:—Copper with currents of 10 amperes at about three volts, lead as peroxide, silver from boiling ammoniacal and acetate solutions, and bismuth.

PHYSICAL SOCIETY.

Annual General Meeting, February 9th, 1906.

Prof. J. H. POYNTING, F.R.S., President, in the Chair.

THE Reports of the Council and the Treasurer were read and adopted.

Report of the Council.

Since the last Annual General Meeting eleven ordinary Science Meetings and two informal meetings of the Society have been held. Of these eleven were held at the Royal

College of Science; one, that on March 24th, was held at University College, and one, on May 26th, at the National Physical Laboratory. The average attendance at the meetings, omitting the informal meeting at the National Physical Laboratory, when no record of the attendance was taken, has been 48.

During the past year the Council departed from the usual programme in setting apart one evening exclusively to an exhibition of apparatus. This innovation was well supported, manufacturers showing a readiness to exhibit, and the attendance of Fellows and visitors was greater than was anticipated, amounting to 240.

The number of Fellows now on the roll is 427, an increase of 3 over the number last year. Fourteen new Fellows have been elected. There have been eight resignations, and the Society has to mourn the loss by death of four Fellows, namely, W. Ackroyd, Rev. H. P. Gurney, Frank McClean, and H. R. Noble.

The number of students now on the roll is 4, the same number as last year. Two new students have been elected. There has been one transfer, and one resignation.

Report of the Treasurer for the Year 1905.

It has been increasingly difficult during the past two or three years to collect arrears of subscriptions, which now stand at a higher figure than usual, presumably in consequence of general depression and excessive taxation. With this exception the position of the Society remains practically unchanged. There is no unusual expenditure to report, except for binding periodicals and for refreshments at the soirée. At the present rate the Society is perhaps leaving rather too narrow a margin for contingencies. Allowing for liabilities the balance is about £10 less than last year, but we may hope that conditions will improve, before the balance is dangerously reduced.

Election of Honorary Fellows.

The following were elected as Honorary Fellows of the Society:—F. Kohlrausch, A. A. Michelson.

Election of Officers and Council.

The following Officers and Council were elected for the ensuing year:—

President—Prof. J. Perry, F.R.S.

Vice-Presidents—Those who have filled the Office of President, together with C. Chree, LL.D., Sc.D., F.R.S.; H. M. Elder, M.A.; Prof. J. A. Fleming, M.A., D.Sc., F.R.S.; and J. Swinburne.

Secretaries—W. R. Cooper, M.A., and Prof. W. Cassie, M.A.

Foreign Secretary—Prof. S. P. Thompson, B.A., D.Sc., F.R.S.

Treasurer—Prof. H. L. Callendar, M.A., LL.D., F.R.S.,
Librarian—W. Watson, D.Sc., F.R.S.

Other Members of Council—T. H. Blakesley, M.A.; A. Campbell, B.A.; W. B. Croft, M.A.; W. Duddell; J. A. Harker, D.Sc.; W. A. Price, M.A.; S. Skinner, M.A.; S. W. J. Smith, M.A.; W. Watson, D.Sc., F.R.S.; Prof. H. A. Wilson, M.A., D.Sc.

Prof. J. PERRY then took the chair and delivered an Address.

He said that in the early days of the Society, when he had the honour of acting as a Secretary, and when Guthrie and Foster, Kelvin and Fitzgerald were Presidents, no Presidential Addresses were delivered, and he questioned whether we were not overdoing the business of requiring general addresses, which must almost always have as their theme the progress of science. Seldom did we find in such addresses new accounts of important original work, and he felt the inappropriateness of such an Address in speaking before a Society whose Proceedings were more intense with original work of the best kind than any other Society known to him with the exception of the Royal Society. He thought that every young reader of a paper before a scientific society made the mistake of assuming that his audience knew a great deal of the subject so familiar to

himself, and hence his paper was not understood. Writers of books on Physics assume their readers to be all truly logical students; they use words properly in a technical sense, and forget that many of their readers may use them in the newspaper writer's sense. For example, take the expression "adiabatic expansion." There are people who insist on finding that Rankine, Maxwell, and all others of our most exact writers are not only inconsistent with one another in the use or the expression, but that each is inconsistent with himself. If a portion of fluid expands slowly without gain or loss of heat, we know the way in which its p , v , and t alter as it changes state; this was originally called "adiabatic expansion," and the term has become a technical term for that kind of alteration of p , v , and t , however it may occur. Steam or air may be throttled through a non-conducting reducing valve, but the expansion is not adiabatic, although there is no gain or loss of heat. Steam or air passing along a pipe with friction, if it can only be made to lose heat through the metal of the pipe at exactly the proper rate at every place, is expanding adiabatically. When it is assumed that steam or air flows without friction from a vessel through an orifice, it is said that the expansion is adiabatic although it is rapid.

Referring to the teaching of physics to students entering upon the engineering profession, the President remarked that such teaching was nearly always slipshod. Many men enter a science college at the age of eighteen or more, knowing nothing of physical science. In the case of a great percentage of such men, it is impossible that they should acquire the scientific habit of thought. It is because so much of this kind of material is dealt with, that much of our teaching is slipshod. Every pupil entering a science college ought to have been experimenting and working graphically and numerically on physical science problems from a very early age, and then our science classes would deal with them in a scientific way. The causes of the unfitness of the average student are two:—One that his instincts and habits of thought were not trained from early youth; the other that his teachers in science colleges have absurd and uninteresting courses of study for him. In physics we are dealing with ideas which are not familiar to young students, ideas which can only become familiar in the laboratory. For example, such a simple mathematical idea as that of a decimal cannot be given in elementary schools in less than five or six years, whereas one week of weighing and measuring would give young children familiarity and clear ideas about decimals. Numerous examples could be given to prove that the principles of physics cannot be understood unless there has been early experimental training, and this is the reason why the professors of science in colleges of university rank and the professors in technical colleges obtain such poor reward for their labours. Referring to the many hundreds who every year take science degrees at the universities, and the thousands who pass the London University Matriculation examination, Prof. Perry remarked that if that was the standard of excellence of those present, his Address could serve no useful purpose. Nothing ought to be compulsory in schools except the study of English and of Natural Science. The object of a matriculation examination is to test whether a student entering a college will be able to benefit by the course of study there. The only language which ought to be compulsory in the Science department of a University is English. A Professor of Science ought to be allowed to teach his students in the way that seems best to him, and he should examine his students himself. Hedge him round with rules and regulations framed by Boards of Studies; tie him down to a syllabus, and the work he will do might be much better, certainly much more cheaply, done by a grinder at low wages. There is no one general elementary course in physics which all students ought to take: neither by their previous training nor from the uses which they will make of the principles of physics are they fit to be taught together. What is wanted is more classes, more rooms, and more teachers.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

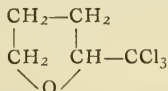
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 4, January 22, 1906.

Ebullition of Osmium, Ruthenium, Platinum, Iridium, Rhodium, and Palladium.—Henri Moissan.—All the metals belonging to the platinum family are easily melted and can be boiled in the author's electric furnace with currents varying from 500 to 700 ampères at pressure of 110 volts. Starting with 150 grms. of metal, fusion takes one or two minutes and regular ebullition is attained in about four minutes. Cold water is allowed to flow through a copper tube which is placed above the crucible in which the experiment takes place. The vapour is condensed on this in metallic drops formed of crystalline layers, each layer consisting of a network of crystals visible only under the microscope. All these metals when in the liquid state dissolve carbon; this latter substance crystallises out on cooling in the form of graphite. Osmium is the most difficult of all the metals to distil. Palladium is more easily fused than platinum, but is apparently less volatile than either platinum or rhodium.

Cathodic Phosphorescence of Europium.—G. Urbain.—The author has extracted europium from monazite sands, xenotime, and pitchblende. The earth prepared from any of these minerals by fractionation of the double magnesium nitrates in presence of excess of an isomorphous bismuth salt, shows a constancy of properties which is in general characteristic of definite elements. He now investigates the cathodic phosphorescence which europium excites when diluted to various degrees with other oxides.

Mixtures of Antimony and Tellurium, Antimony and Selenium, Cryoscopic Constancy of Antimony.—H. Pelabon.—Under the action of heat tellurium combines directly with antimony, forming a kind of mixture of the two bodies, consisting of antimony telluride accompanied by an excess of one or other of the elements. The mixtures thus obtained melt at temperatures below 620° and give homogeneous liquids, which, differing from antimony sulphide, do not separate into two superposed layers. The author investigates the solidification of these liquids and traces the curve of fusibility.

Methoxytrichloropentanol-1.5.4 and α -Trichloromethyltetrahydrofurfuran.—J. L. Hamonet.—Continuing his researches on the halogen ether oxides, $RO(CH_2)_nX$, the author investigates the reaction of anhydrous chloral on the magnesium derivative of iodomethoxypropane-1.3. The principal product of the reaction is methoxytrichloropentanol-1.5.4, $CH_3O.CH_2.CH_2.CH_2.CH.OH.CCl_3$. He examines the properties of this body and distils a mixture of it and phosphoric anhydride. The experiment is performed in a vacuum in a paraffin bath, and, by removal of a molecule of methanol, α -trichloromethyltetrahydrofurfuran,—



is obtained.

Acetylenic Amides and Nitrites.—Ch. Moureu and I. Lazennec.—In this preliminary note the authors give an account of the preparation and general properties of certain acetylenic amides. When hot, alcoholic potash saponifies these amides, giving the corresponding acetylenic acid, $R-C\equiv C-CO_2H$. By hydration, this is transformed more or less completely into β -ketonic acid, $R-CO-CH_2-CO_2H$, and then into the corresponding acetone, $R-CO-CH_3$, or acid, $R-CO_2H$.

Glycidic Condensation of Aldehydes with α -Chloropropionic Ether.—Georges Darzens.—In the fatty series, the author prepares the $\alpha\beta$ -disubstituted glycidic ethers of the type $R-CH-C\begin{smallmatrix} \nearrow CH_3 \\ \searrow O \end{smallmatrix}-CO_2C_2H_5$ by condensing acet-

aldehyde, propylic aldehyde, and isovaleric aldehyde, but the yields are always very small (20 to 30 per cent at the most). Saponification of these ethers gives relatively stable acids. On the contrary the aromatic aldehydes give very good yields, and the glycidic acids thus prepared decompose sharply into carbon dioxide and ketones of the type $R-CH_2-CO-CH_3$.

NOTES AND QUERIES.

Examination Questions.—Can any reader recommend a book of Questions on Inorganic Chemistry suitable for revising before an examination? If possible, I should like one with a key, and comprising the whole subject as dealt with in such books as Shennstone's "Inorganic Chemistry," but I should very much like to know of one which comes as near to this as possible.—A. U.

MEETINGS FOR THE WEEK.

- MONDAY, 26th.—Society of Arts, 8. (Cantor Lectures). "Modern Warships," by Sir William White, F.R.S., &c.
TUESDAY, 27th.—Royal Institution, 5. "Food and Nutrition," by Prof. William Stirling, M.D., &c.
WEDNESDAY, 28th.—Society of Arts, 8. "London Traffic," by Capt. G. S. C. Swinton.
THURSDAY, Mar. 1st.—Royal Institution, 5. "The Physiology of Plants," by Francis Darwin, M.A., &c.
Chemical, 8.30. "Studies of Dynamic Isomerism—Part IV., Stereoisomeric Halogen Derivatives of Camphor," by T. M. Lowry.
FRIDAY, 2nd.—Royal Institution, 9. "Hippocrates and the Newly Discovered Health Temple at Cos," by Richard Caton, M.D., &c.
SATURDAY, 3rd.—Royal Institution, 3. "The Corpuscular Theory of Matter," by Prof. J. J. Thomson, F.R.S., &c.



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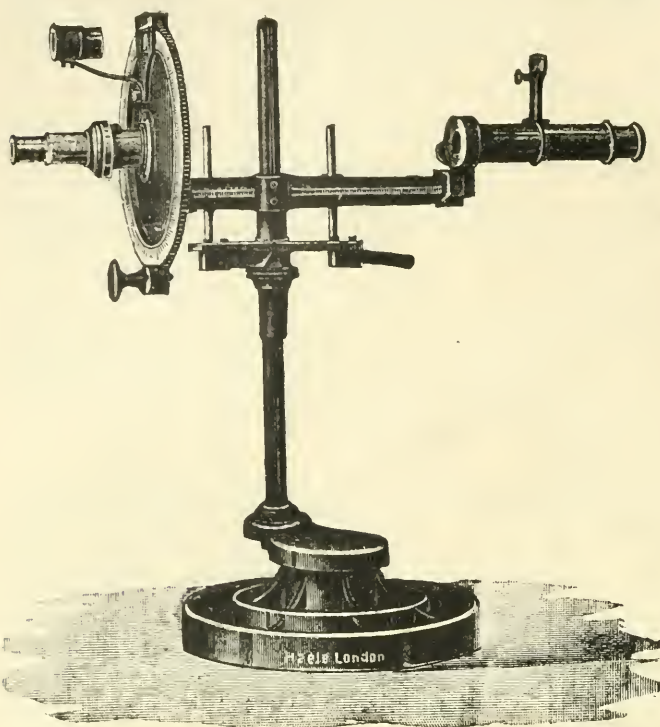
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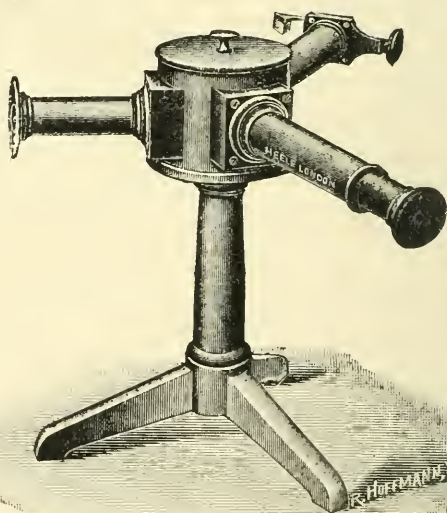
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THE CHEMICAL NEWS.

VOL. XCIII., No. 2414.

GALVANIC CELLS PRODUCED BY THE ACTION OF LIGHT.*

(SECOND COMMUNICATION).

THE CHEMICAL STATICS AND DYNAMICS OF REVERSIBLE AND IRREVERSIBLE SYSTEMS UNDER THE INFLUENCE OF LIGHT.

By MEYER WILDERMAN, Ph.D., B.Sc. (Oxon.).

THE following is a summary of the different subjects dealt with in the paper:—

1. Further evidence is given that velocity of chemical reaction and chemical equilibrium in homogeneous systems follow under the action of light the laws of mass action.

2. Experimental proof that the E.M.F. produced by light in the different systems consists of two E.M.F.'s, viz., one created by light at a constant temperature due to the variation of chemical potential, and a thermo-E.M.F. simultaneously produced by the heating effect of the light, and due to the variation of the chemical potential with temperature (quantitative separation of the total E.M.F. into the two E.M.F.'s, and determination of the value of each E.M.F. in the different systems).

3. Experimental proof that the rays of all wave-lengths act both "chemically" and as "heat rays," only in different degrees.

4. Dealing with the experiments of Becquerel and Minchin, it is shown that phenomena observed by Becquerel and Minchin are not surface phenomena, but that their combination forms inconstant galvanic cells under the action of light. Experimental proof. Polarisation. (Influence of composition of the heterogeneous system upon its properties, as constant or inconstant galvanic cells. The course of the parts of the curves giving the induction and deduction periods in constant and inconstant cells).

5. On the nature of the chemical processes in galvanic cells created by light.

6. The method of investigation. The general arrangements of the experiments. The arrangements of a constant acetylene and arc light, of the photometer, the quartz vessel, the preparation of the plates, the bath. Arrangements for calibration of the obtained results in standard units for photographing the effect of light upon different systems, &c.

7. On the E.M.F.'s in the dark, gas batteries, &c.

8. Chemical statics and dynamics of constant cells reversible in respect of the cation (e.g., Ag plates in NO_3Ag solution). The composition of such a system. The reactions going on in such a system. Proof that this system is reversible, that its composition remains constant under the action of the current, that the galvanic cells are *sui generis*. The relationship to Gibb's rule of phases.

9. Experimental results obtained with constant cells reversible in respect of the cation. The constant deflections in light. The course of the deduction and induction periods. The law of intensity. The E.M.F. obtained with the same system on extension of the experiments for longer periods. Influence of the composition of light upon the E.M.F. obtained (coloured screens). Influence of concentration of the solution upon the E.M.F. obtained.

10. The physico-mathematical theory of constant cells reversible in respect of the cation. The deduction of the general equation from the maximum work done by the system under the action of light (see *Roy. Soc. Proc.*, 1905). An experimental test and verification of the same in all its details. The E.M.F. and intensity of light. The

analogy between the action of heat and of light upon the systems, following from the direction of the current when the same plate is heated or illuminated (at a constant temperature); the author's "principle of movable equilibrium for light."

11. Chemical statics and dynamics of constant cells reversible in respect of the anion (e.g., Ag-BrAg plates in NaBr solution). The composition of such a system. The reactions going on in such a system. The mechanism of the reactions. Proof that such a system is reversible, that its composition remains constant under the action of the current, that they are *sui generis* (points of difference from ordinary galvanic cells). The relationship to Gibb's rule of phases.

12. Experimental results with constant cells reversible in respect of the anion, the course of the induction and deduction periods, the law of intensity, influence of composition of light (coloured screens). Acetylene and arc. Influence of concentration of the solution, influence of temperature, influence of the cation, transformation of constant cell into inconstant cells under the action of light, and vice versa, the role of the electrode in light cells. Experimental determination of the electrical potentials between the illuminated and not illuminated parts of the solution; what is to be understood under "the electrode reversible in respect of the anion"; on the conditions, under which constant reversible galvanic cell can be obtained, &c.

13. The physico-mathematical theory of constant cells reversible in respect of the anion. A detailed theoretical and experimental investigation similar to that in 10.

14. On the E.M.F. of constant reversible cells and the intensity of light (Experimental proof).

15. Chemical velocity of reaction in homogeneous systems when they are shifted to a new point of equilibrium by light at a constant temperature, follows, after the induction period has passed, the same law of mass action as in the dark. Further extensive experimental confirmation given by "galvanic cells created by light."

16. Chemical equilibrium in heterogeneous systems when shifted by light at a constant temperature to a new point, follow, after the induction period has passed, the same laws as in the dark.

17. The maximum work (containing the constant of equilibrium) and the law of intensity. Experimental proof that in homogeneous systems—

$$RT \ln \frac{C_1^m C_2^{n_2} \dots}{C_3^{m_3} C_4^{n_4} \dots} = RT \ln K = RT \ln \frac{k_1}{k_2} = C.I;$$

where k_1 , k_2 , are the velocity constants, K the constant of equilibrium.

18. The connection between the velocity of chemical reaction produced by the action of light, the intensity of light and absolute temperature; (a) when both reactions go on under the action of light only—

$$RT \ln K_1 = C''I \text{ or } C''I + (k) \text{ and } RT \ln K_2 = C'''I \text{ or } C'''I + (k),$$

(b) if only one reaction goes on in light, the other also in the dark,—

$$RT \ln k_1 = C''I + RT \ln k_2.$$

At a constant temperature—

$$\ln k_1 = C.IV.I + K.IV.$$

19. The velocity of molecular or physical reactions between different parts of the heterogeneous system produced by and going on only under the action of light, follow the law found by the author for those reactions in the dark (*Report British Association*, Liverpool; *Zeit. Physik. Chem.*, 1899, vol. xxx., pp. 348—368).

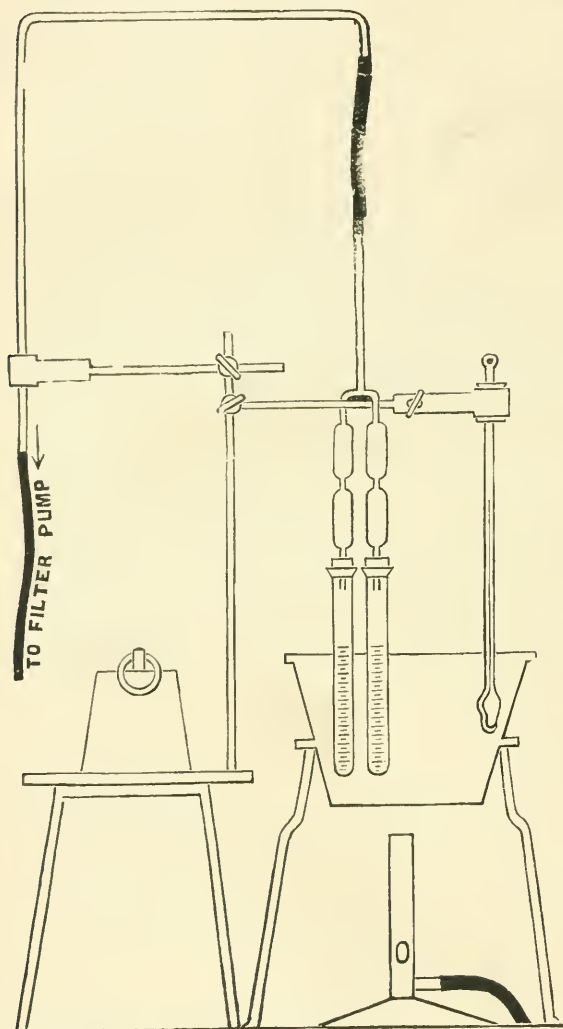
20. Velocity of chemical reaction in heterogeneous systems produced by and going on only under the action of light follow, after the induction period has passed, the laws deduced by the author for velocity of chemical reaction in heterogeneous systems in the dark (*Zeit. Physik. Chem.*, 1899, vol. xxx., pp. 371—382; *Phil. Mag.*, 1902, [6], pp. 468—489).

* Abstract of a Paper read before the Royal Society, January 25, 1906.

FURTHER EXPERIMENTS ON A NEW METHOD
OF DETERMINING MOLECULAR WEIGHTS.*

By PHILIP BLACKMAN.

It was found that, with solvents of fairly high boiling-points, no results could be obtained with the apparatus and method described by the author in *Journal of the Chemical Society*, 1905 (*Trans.*, lxxxvii., 1474), the boiling being extremely violent and irregular. The attempt was then made to carry out the operations under reduced pressure (this being effected by connecting the free end of the



T-piece with a filter-pump), and the results were much more satisfactory. It was found that most of the evaporated solvent, instead of escaping, condensed in the upper (cooler) portions of the apparatus, the condensed liquid remaining in the bulbs (the soft rubber tubing employed often collapsed, and this alone would have prevented any very considerable quantity of vapour escaping). In reading the volumes of the solutions care had to be taken that the solvent in the bulbs did not flow back into the test-tubes. No difficulty was met with in doing this,

for, on raising the apparatus from the water-bath, the excess of pressure within the test-tubes over that in the bulbs was quite sufficient to prevent the liquid in the bulbs from returning to the tubes for a considerable time.

Danger of ejection of the solution or of mixing, caused by any violent ebullition, will be obviated by having two bulbs instead of one in each of the limbs of the T-piece. The lower the boiling-point of the solvent employed, the easier will it be to carry out the determinations, and the more reliable will the results be.

A condenser should not be employed with the apparatus (compare *Trans.*, 1905, lxxxvii., 1476, Precaution 8), as not only will it destroy the mobility of the apparatus (as the latter would have to be firmly clamped to prevent it overturning), but it will also render it liable to break.

Experiments were carried out by conducting air at the same rate through the solutions, but the results were not satisfactory.

Results.

In the following experiments, a filter-pump and a water-bath were always used; also, instead of platinum wire, small pieces of broken glass (of inappreciable volume) were employed to assist in regulating the boiling.

After the first reading (No. 1), taken when a considerable quantity of liquid had collected in the bulbs, the liquid was allowed to flow back into the test-tubes. A second reading (No. 2) was then taken when a fair amount of liquid had again condensed in the bulbs. This process was repeated as often as was convenient.

- I. Compared *p*-dibrombenzene (m_1, v_1) with 1-chlor-2,4-dinitrobenzene (m_2, v_2). Equal weights of each (0.07 gm.); solvent, alcohol (96 per cent); time, thirty minutes; ebullition, steady.

$$m_1/m_2 = 236/202 = 1.168.$$

No.	v_1 . C.c.	v_2 . C.c.	v_2/v_1 .
1.	7.3	8.5	1.16
2.	7.0	8.2	1.17
3.	6.5	7.6	1.16
4.	6.0	7.0	1.16
5.	5.5	6.5	1.17

- II. Compared *p*-chlornitrobenzene (m_1, v_1) with benzil (m_2, v_2). Equal weights (0.08 gm. each); solvent, alcohol (96 per cent); time, thirty minutes; ebullition steady.

$$m_2/m_1 = 210/157 = 1.337.$$

No.	v_1 .	v_2 .	v_1/v_2 .
1.	8.5	6.5	1.31
2.	8.4	6.3	1.33
3.	8.0	6.0	1.33
4.	7.4	5.5	1.34
5.	7.1	5.2	1.34

- III. Compared *p*-nitraniline (m_1, v_1) with *p*-nitrobenzoic acid (m_2, v_2). Equal weights of each (0.07 gm.); solvent, alcohol (96 per cent); time, twenty minutes; ebullition regular.

$$m_2/m_1 = 167/138 = 1.21.$$

No.	v_1 .	v_2 .	v_1/v_2 .
1.	8.4	7.0	1.20
2.	8.3	6.8	1.22
3.	8.0	6.6	1.21
4.	7.5	6.1	1.23

- IV. Compared *p*-nitraniline (m_1, v_1) with hydroquinone (m_2, v_2). Equal weights (each 0.08 gm.); solvent, alcohol (96 per cent); time, thirty-five minutes; ebullition steady.

$$m_1/m_2 = 138/110 = 1.25.$$

* A Paper read before the Chemical Society, December 21, 1905.

No.	v_1 . C.c.	v_2 . C.c.	v_2/v_1 .
1.	6.8	8.2	1.21
2.	6.3	7.7	1.22
3.	5.7	7.3	1.28
4.	5.5	7.0	1.27
5.	5.0	6.3	1.26
6.	4.8	6.0	1.25

V. Compared *p*-nitrotoluene (m_1, v_1) with *p*-dibrombenzene (m_2, v_2). Equal weights of each (0.1 grm.); solvent, alcohol (96 per cent); time, twenty minutes; ebullition somewhat unsteady.

$$m_2/m_1 = 236/137 = 1.72.$$

No.	v_1 .	v_2 .	v_2/v_1 .
1.	6.5	3.7	1.75
2.	6.0	3.4	1.76
3.	5.4	3.1	1.74

VI. Compared phenolphthalein (m_1, v_1) with *p*-resorcylic acid (m_2, v_2). Equal weights (each 0.09 grm.); solvent, alcohol (96 per cent); time, twenty minutes; ebullition somewhat irregular.

$$m_1/m_2 = 318/154 = 2.06.$$

No.	v_1 .	v_2 .	v_2/v_1 .
1.	3.7	7.5	2.03
2.	3.3	7.0	2.12
3.	3.5	7.2	2.06

VII. Compared 1-brom-3.4-dinitrobenzene (m_1, v_1) with hydrazobenzene (m_2, v_2). Equal weights (0.07 grm. each); solvent, alcohol (96 per cent); time, twenty-five minutes; after fourth reading the boiling became violent.

$$m_1/m_2 = 247/184 = 1.34.$$

No.	v_1 .	v_2 .	v_2/v_1 .
1.	6.0	8.0	1.33
2.	5.8	7.8	1.34
3.	5.5	7.3	1.33
4.	5.2	7.0	1.34

VIII. Compared phenolphthalein (m_1, v_1) with *p*-cresotinic acid (m_2, v_2). Equal weights (each 0.1 grm.); solvent, alcohol (96 per cent); time, thirty minutes; ebullition regular.

$$m_1/m_2 = 318/152 = 2.09.$$

No.	v_1 .	v_2 .	v_2/v_1 .
1.	4.0	7.5	1.87
2.	3.5	6.9	1.97
3.	3.4	6.8	2.00
4.	2.8	5.8	2.07
5.	1.0	2.0	2.00

IX. Compared iodoform (m_1, v_1) with *m*-cresotinic acid (m_2, v_2). Equal weights of each (0.1 grm.); solvent, alcohol (96 per cent); time, twenty minutes; after third reading boiling became violent.

$$m_1/m_2 = 394/152 = 2.59.$$

No.	v_1 .	v_2 .	v_2/v_1 .
1.	3.6	8.0	2.22
2.	2.5	5.8	2.32
3.	3.0	7.5	2.50

X. Compared *p*-amidophenol (m_1, v_1) with α -naphthol (m_2, v_2). Equal weights (0.1 grm. each); solvent, alcohol (96 per cent); time, fifteen minutes; after second reading boiling became very violent.

$$m_2/m_1 = 144/109 = 1.32.$$

No.	v_1 .	v_2 .	v_2/v_1 .
1.	6.2	5.0	1.24
2.	6.0	4.8	1.25

XI. Compared 1-brom-3.4-dinitrobenzene (m_1, v_1) with *o*-cresotinic acid (m_2, v_2). Equal weights of each (0.07 grm.); solvent, benzene (boiling-point 80—82°); time, one hundred and seventy minutes; ebullition slightly irregular.

$$m_1/m_2 = 247/152 = 1.62.$$

No.	v_1 . C.c.	v_2 . C.c.	v_2/v_1 .
1.	5.5	7.5	1.36
2.	5.0	7.0	1.40
3.	3.5	6.0	1.71
4.	3.0	5.0	1.66
5.	5.0	8.0	1.60
6.	4.0	6.0	1.50
7.	4.0	6.2	1.55
8.	3.5	6.0	1.71
9.	3.0	5.2	1.73
10.	4.5	7.0	1.55
11.	3.5	6.0	1.71
12.	3.3	5.8	1.76
13.	3.5	6.0	1.71

XII. Compared *p*-cresotinic acid (m_1, v_1) with cinnamic acid (m_2, v_2). Equal weights of each (0.07 grm.); solvent, benzene (boiling-point 80—82°); time, twenty minutes; ebullition somewhat unsteady.

$$m_1/m_2 = 152/148 = 1.03.$$

Volumes v_1 and v_2 were nearly always equal, giving $v_2/v_1 = 1.0$ approximately.

XIII. Compared hydrazobenzene (m_1, v_1) with *m*-cresotinic acid (m_2, v_2). Equal weight of each (0.07 grm.); solvent, benzene (boiling-point 80—82°); time, forty minutes; ebullition somewhat irregular.

$$m_1/m_2 = 182/152 = 1.19.$$

No.	v_1 .	v_2 .	v_2/v_1 .
1.	6.0	7.3	1.21
2.	5.5	6.6	1.18
3.	4.5	5.8	1.29
4.	4.0	5.0	1.25
5.	3.7	4.5	1.21
6.	3.3	4.1	1.24
7.	3.0	3.6	1.20

XIV. Compared phenolphthalein (m_1, v_1) with diphenylamine (m_2, v_2). Equal weights of each (0.08 grm.); solvent, acetone (boiling-point 56.5—57°); time, forty-five minutes; ebullition steady.

$$m_1/m_2 = 318/169 = 1.88.$$

No.	v_1 .	v_2 .	v_2/v_1 .
1.	4.4	7.6	1.73
2.	3.8	7.2	1.89
3.	3.4	6.7	1.97
4.	1.8	3.4	1.88
5.	3.2	6.0	1.87
6.	2.7	5.1	1.88
7.	2.0	3.6	1.80
8.	2.2	3.8	1.73

XV. Compared *p*-dibrombenzene (m_1, v_1) with *p*-nitrotoluene (m_2, v_2). Equal weights of each (0.08 grm.); solvent, acetone (boiling-point 56.5—57°); time, forty minutes; ebullition steady.

$$m_1/m_2 = 236/137 = 1.72.$$

No.	v_1 .	v_2 .	v_2/v_1 .
1.	4.0	7.0	1.75
2.	3.7	6.7	1.81
3.	3.5	6.3	1.80
4.	3.3	6.0	1.82
5.	3.0	5.3	1.77
6.	2.5	4.5	1.80
7.	2.8	5.0	1.78

THE RADIO-ACTIVITY OF THE URANYL
DOUBLE SALTS.

By W. MARCKWALD.

THE remarkably great radio-activity of certain uranyl double salts has recently been mentioned in several publications. R. J. Meyer and Fritz Wendel (*Berichte*, 1903, xxxvi., p. 4655) first called attention to the fact that potassium and ammonium uranyl nitrate "have powerful radio-active effects upon the photographic plate." E. Rimbach (*Berichte*, 1904, xxxvii., p. 461) went into this question rather more deeply. With H. Bürger and A. Grewe he investigated many uranyl double nitrates, chlorides, and sulphates with alkalis and other bases, and he found that most of the salts examined produced no blackening of the photographic plate after exposures of twelve hours. "But a strong effect was produced with the potassium and rubidium double sulphate, and most of all with the double nitrates of potassium, ammonium, and rubidium." Rimbach's fellow worker, A. Grewe, in his Dissertation "Beiträge zur Kenntniss der Doppelsalze im Unwandelungsintervall," Bonn, 1905, describes more extensive experiments on radio-activity, especially that of uranyl potassium nitrate, compared with uranyl nitrate. He compared the radio-activity of the two salts not only by means of the photographic plate, but also with an electroscope, and came to the conclusion that the activity of the salts in the latter case was of the same order of magnitude, but that, on the other hand, the double salt had a powerful effect upon the photographic plate in twenty-four hours, while the action of uranyl nitrate itself was hardly appreciable.

The fundamental experiments of H. Becquerel and of P. and S. Curie on the radio-activity of uranium and its compounds showed that in the many uranium compounds which they investigated the strength of the activity corresponds approximately to the amount of uranium the compound contains. This fact is one of the most important supports of Rutherford's theory of the cause and nature of radio-activity, which has proved so fruitful. It is clear that the foundations of our theoretical views would be destroyed if the assumption of the above authors should prove to be correct, that certain uranium compounds could possess a higher radio-activity than uranium itself.

For this reason it appeared of interest to investigate this question thoroughly. Dr. R. J. Meyer was kind enough to place his preparations at my disposal, for which I owe hearty thanks to him, and also to Dr. H. Grossman, who sent me two ethylene diamine double salts of uranyl which had not yet been described, namely, the sulphate and nitrate, the latter of which exhibited an abnormally strong action upon the photographic plate.

Besides these two ethylene salts, I have examined uranyl potassium nitrate, uranyl thallium nitrate, and a specimen of uranium nitrate used to prepare these salts. The activity of the salts was first determined quantitatively in the usual way by means of a sensitive electrometer, and was found to be of the same order of magnitude for all the salts. As the quantities of the salts at my disposal enabled me to spread them out over a surface of 16 sq. c.m. only, the measured saturation current was too small to allow the more minute differences to be detected. It amounted to about $0.2 \cdot 10^{-11}$ ampères. These measurements confirmed and supplemented Grewe's observations with the electroscope. Hence the α -radiation of all the salts examined is approximately the same as the theory requires.

The question now occurred whether the β -radiation would show considerable differences. The above mentioned authors, with the exception of Grewe, have not expressly stated that in their photo-chemical experiments they protected the sensitive plate from the action of light by means of opaque paper. Only Grewe mentions that the action of potassium uranyl nitrate on the photographic plate is not perceptibly lessened by means of opaque paper. This

latter statement, according to my experiments, is undoubtedly founded on an error.

A photographic plate was wrapped in opaque paper in such a way that there was a single layer of paper on the film side. On this pieces of glass, lead wire, and thin aluminium foil were distributed, and the five above mentioned salts contained in thin walled little glass vessels were laid directly on these. After twenty-four hours the plate was developed. With all the salts the action was uniformly very small, and scarcely perceptible. When the experiment was repeated under the same conditions, except that the plate was exposed for six days, it was distinctly blackened wherever the salts had lain. The pieces of glass and lead appeared as brighter images, while the aluminium, which is easily penetrated by β -rays, was more faintly indicated. In this case also the action of all five salts was about the same. Hence no considerable difference can be established in the β -radiation of the five salts.

The result was totally different if the salts in the little glass vessels were laid directly on the photographic plate. After twenty-four hours the plate appeared strongly blackened where the potassium uranyl nitrate and the ethylene diamine uranyl nitrate had been, while, on the other hand, the action of the uranyl nitrate, of the thallium uranyl nitrate, and ethylene diamine uranyl sulphate was distinct, but very much fainter. It follows from the foregoing that the effect is produced by the action of light rays but not Becquerel rays, and this was seen still more clearly when pieces of glass, opaque paper, and aluminium were laid on the photographic plate, and the glass vessels on these. The glass, which was 1.5 m.m. thick, was penetrated by the active rays without any diminution in strength, while on the contrary the paper and aluminium, which were 0.2 m.m. thick, threw sharp shadows.

This result thus shows that the above uranium salts emit light rays, and the potassium and ethylene diamine double nitrate to a much higher degree than the other salts. Both the double salts differ from the three others externally because of their strikingly beautiful fluorescence. This power of luminescence can be due to one of two causes. The most obvious explanation would be to suppose that these salts, like other phosphorescent substances, emit light for a long time after they have been illuminated. However, the photo-chemical action of these salts is not diminished even after they have been kept in the dark for weeks. Thus there only remains the assumption that in the fluorescing uranium salts part of the Becquerel radiation is converted into light energy, and this conversion is greater the more strongly the salts fluoresce.—*Berichte*, 1906, xxxix., p. 200.

ANALYSIS OF ALLOYS OF COPPER.*

By JOHN M. WILSON,
Assistant Inspector of Engineering Material, U.S.N.

(Concluded from p. 85).

Phosphor Bronze.

WEIGH 1 grm. into a No. 1 beaker, dissolve in 5 c.c. concentrated HNO_3 , warm on a steam plate till free from nitrous fumes, and add 25 c.c. water. Warm until precipitated SnO_2 is white, filter, wash with HNO_3 (1 to 10), and electrolyse for copper and lead.

Weigh 5 grms. into a No. 3 beaker, add 25 c.c. concentrated HNO_3 , and heat till free from nitrous fumes. Add 75 to 100 c.c. water, digest till insoluble matter is white, filter through a double filter, and wash copper salts out with HNO_3 (1 to 10). Put filter and precipitate in an Erlenmeyer flask, add 25 c.c. $(\text{NH}_4)_2\text{S}$, digest two to three hours in the cold, shaking occasionally, and heat on steam-plate for one hour. Filter, wash out all alkaline sulphides,

* The Chemical Engineer, ii., No. 3.

add 20 to 25 c.c. magnesia mixture, and shake occasionally for twenty minutes. Add one-sixth volume concentrated NH_4OH , shake well, allow to stand over-night, and filter into a 500 c.c. graduated flask. Wash out all $(\text{NH}_4)_2\text{S}$, dissolve, precipitate in HCl , and re-precipitate with NH_4OH . Add 100 c.c. $(\text{NH}_4)_2\text{S}$, digest on steam-table for one hour, add $\frac{1}{2}$ volume of NH_4OH , allow to stand several hours, filter into the same flask, wash thoroughly, and take up in HCl . Evaporate to dryness, moisten with HCl , take up in water, add H_2SO_3 , boil, saturate with H_2S to get rid of any possible As , filter, and evaporate off H_2S . Cool thoroughly, add NH_4OH till neutral, shake vigorously, keeping the liquid cold, and add NH_4OH , drop by drop, until the precipitate forms. Set aside fifteen minutes, shaking occasionally, and add one-sixth its volume of NH_4OH . Shake vigorously, allow to stand at least four hours, filter on a weighed Gooch felt, wash with NH_4OH (1 to 3) containing NH_4NO_3 , dry at 100°C , ignite, and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$. Calculate to P .

Make the sulphide filtrate up to mark and mix thoroughly, take 100 c.c. (equivalent to 1 gm.), add 1 to 2 grms. KClO_3 , and then 25 c.c. concentrated HCl . Digest on the steam-plate, adding KClO_3 if required, until the separated sulphur is a clear yellow colour, filter through glass-wool, and wash with hot water. Transfer to a No. 3 beaker (volume 200 to 250 c.c.), add a slight excess of NH_4OH , and then 10 grms. $\text{H}_2\text{C}_2\text{O}_4 + 10$ grms. $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Warm till a clear solution is obtained, and electrolyse over-night with a current of 5 c.c. electrolytic gas per minute. Wash, dry, and weigh the electrode as for copper. The weight represents the tin. Iron is to be determined as in manganese bronze.

Babbitt Metal and White Metals.

For the analysis of these metals one of two methods is used, according to the quantity of lead present.

Little Lead Present.

Five grms. of cuttings are weighed into a 5-inch dish, concentrated, 50 c.c. HNO_3 are added, and when violent action ceases, the solution is evaporated to dryness on the steam-table. The dry powder is moistened with 20 per cent NaOH , 10 to 20 c.c. being required, 40 c.c. of Na_2S is added, and after boiling one hour 80 c.c. water is also added. The residue is allowed to settle, the clear liquid is decanted as much as possible into an Erlenmeyer flask, and the digestion repeated twice, using 30 c.c. and 20 c.c. Na_2S respectively. The solution is then filtered through a double filter, or preferably a pulp filter as recommended by Shimer, washing out all alkaline sulphides with cold water, keeping the filter completely filled with wash all the time. When washed the filter is allowed to drain. Dead roast the precipitate in porcelain, dissolve in HNO_3 , and electrolyse the copper and lead.

Make the residual liquid and washings in the Erlenmeyer flask slightly alkaline, warm, and precipitate with H_2S . Cork flask and allow to stand over-night. Filter through paper, wash with water containing $(\text{NH}_4)_2\text{S}$, and dissolve soluble sulphides in a mixture of 1 volume HCl and 4 of H_2S water. Wash with cold water, ignite, and weigh precipitate. Test to ascertain whether it is copper or nickel.

Evaporate the solution of soluble sulphides to dryness, moisten with HCl , add a few drops HNO_3 , and again evaporate to dryness. Take up with HCl and water, precipitate the iron three times with NH_4OH , and dissolve the precipitate in H_2SO_4 . Reduce, and titrate the iron.

Saturate the cold united filtrates with H_2S , allow to stand over-night, filter through a double filter. Wash with cold water, ignite in porcelain, and weigh as ZnO . Calculate to zinc.

Make alkaline sulphide solutions up to volume, mix thoroughly, and take out four portions:—Two of 50 c.c. each (equivalent to $\frac{1}{2}$ gm.), and one of 25 c.c. (equivalent to $\frac{1}{4}$ gm.), and one of 20 c.c. (equivalent to $\frac{1}{5}$ gm.).

The 20 and 25 c.c. portions are to be oxidised with

$\text{HCl} + \text{KClO}_3$ and electrolysed for tin exactly as described under phosphor bronze.

The antimony is determined either (a) by Clarke's method modified, or (b) by Lord's method modified, or both.

(a). *Clark's Method*.—Dilute the 50 c.c. portion to 400 c.c., add 30 grms. $\text{C}_2\text{H}_4\text{O}_2$, heat on steam-table until all dissolves except a few flocks of Sb_2S_3 , boil ten minutes, and pass a rapid current of H_2S for twenty minutes. Allow to stand in a warm place until the odour of H_2S is nearly gone. Filter through paper, wash with hot water, test filtrate for any unprecipitated antimony. Wash precipitate back into beaker in which it was made, place beaker under funnel, dissolve adhering Sb_2S_3 from paper with a few drops NaOH (1 to 20), and reserve the filter (do not wash). Add 10 to 15 c.c. NaOH (1 to 10) to contents of beaker, warm till all Sb_2S_3 is in solution, filter through the same filter, wash well with hot water, and add 20 grms. $\text{C}_2\text{H}_4\text{O}_2$. Repeat the precipitation. Filter and repeat the solution and precipitation, filter finally on asbestos felt in a small carbon tube, wash with hot H_2O , then with alcohol, then with CS_2 , then with alcohol, and finally with ether. Dry at 100°C , and introduce carbon tube into a large straight tube. Close end of this tube with a stopper carrying a bent delivery tube, and pass a current of CO_2 through it. Heat to 300°C , when S is given off and the precipitate turns black. When no more S is given off cool in the streams of CO_2 and weigh Sb_2S_3 . Calculate to antimony.

(b). *Lord's Method*.—Dilute the 50 c.c. portion to 400 c.c. Add a slight excess of HCl , allow to settle, filter through a double filter. (A Shimer pulp filter would answer better here for convenience in subsequent handling). Wash with water containing $(\text{NH}_4)_2\text{H}_2\text{C}_2\text{O}_4$. Remove precipitate as far as possible with a spatula to the beaker in which it was made, dissolve adhering precipitate with a few drops NaOH (1 to 10), and wash once with water, keeping the volume down. Add enough NaOH (1 to 10) to dissolve precipitate, filter through the same filter into a No. 2 beaker, and wash the filter thoroughly with water, keeping volume below 80 c.c. If more than that volume evaporate to 80 c.c., add one stick solid NaOH (about 10 to 15 grms.), and when dissolved, cool solution. Add 3 c.c. liquid bromine, allow to stand at laboratory temperature over-night, and in the morning place a drop of the solution on the cover. Add a drop of HCl , and if bromine fumes are given off proceed as below; if not add more bromine and digest two to three hours, test again.

When sufficient bromine is present warm on the steam-table one hour and then boil ten minutes. Cool, add one-third its volume of alcohol (95 per cent), stir well, and allow to stand over-night.

Filter through paper, and wash with a mixture of alcohol, water, and Na_2CO_3 . Dissolve precipitate in $\text{HCl} + \text{C}_4\text{H}_6\text{O}_6$, dilute to 300 c.c., add 10 grms. $\text{C}_2\text{H}_4\text{O}_4$, boil and saturate with H_2S by passing a rapid current for twenty minutes. Filter through paper, dissolve in NaOH , re-precipitate the Sb_2S_3 with $\text{C}_2\text{H}_4\text{O}_4 + \text{H}_2\text{S}$, filter through asbestos felt in carbon filtering tube, wash with hot water, alcohol, CS_2 , alcohol and ether, dry at 100°C , heat to 300°C in current of CO_2 in a larger tube, cool in CO_2 , and weigh Sb_2S_3 as directed before. Calculate to antimony.

Both of the above methods give accurate results after the conditions have been mastered, and the results obtained by them check beautifully.

II. When much lead is present I use a method proposed by Mr. G. W. Thompson in "Stillman's Engineering Chemistry."

Weigh 1 or more grms. of cuttings into a beaker, add 80 c.c. per gm. taken of the solvent for white metals given above, evaporate to a syrup, cool rapidly with constant stirring, and add 100 c.c. alcohol (95 per cent), stirring the while. Allow to stand twenty minutes, filter, and wash with a mixture of $\text{HCl} + \text{alcohol}$. Dissolve the precipitate in hot water and $(\text{NH}_4)_2\text{H}_2\text{C}_2\text{O}_4$, warm, boil the solution, and precipitate and weigh the lead as PbCrO_4 .

Evaporate filtrate to dryness, moisten with 10 to 20 c.c. NaOH (10 per cent), add 20 to 40 c.c. H_2O_2 , warm on steam-table for twenty minutes, and add 10 to 20 grms. $C_2H_2O_4$ and 300 c.c. water. Boil the solution, and pass a rapid stream of H_2S through it for twenty minutes. Filter and wash with hot water. Wash the precipitate back into the beaker in which it was made, run 20 c.c. NaOH (1 to 20) through the filter, and wash the latter once with water. Reserve the filter, and add more NaOH to the filtrate and digest on the steam-table until the precipitate has lost all red colour and is quite black. Filter through the same filter, washing thoroughly with water, and dilute the filtrate to 300 c.c. Add 10 grms. $C_2H_2O_4$, heat till all is dissolved except a few flocks of Sb_2S_3 , boil, saturate the solution with H_2S for twenty minutes, and filter on asbestos in a carbon filtering tube. Wash, ignite in CO_2 as above, weigh, and calculate to antimony. Unite the oxalate filtrates, make up to volume, take a suitable portion, and electrolyse for tin.

Burn the black precipitate in porcelain, react until free from sulphur, dissolve in HNO_3 , electrolyse for copper and lead, and in the residual liquid determine iron, zinc, &c.

COMPARISON OF A
WET AND CRUCIBLE-FIRE METHODS FOR
THE ASSAY OF GOLD TELLURIDE ORES,
WITH NOTES ON THE
ERRORS OCCURRING IN THE OPERATIONS
OF FIRE ASSAY AND PARTING.*

By W. F. HILLEBRAND and E. T. ALLEN.

INTRODUCTION.

THE scorification assay for telluride ores has long been believed, and apparently proved, to give low results by reason of volatilisation, and it is now seldom used for ores of that class. The assay by crucible is supposed to be far more reliable, and Furman maintains that it is entirely so when properly carried out ("Manual of Practical Assaying," 1899, p. 399). He gives a very few comparative determinations by fire and wet assay in proof of his assertion, but the tests are too few in number and the agreement is not so close as might be desired. A more critical investigation of this problem seemed to promise results of some value to those engaged in mining and smelting the telluride ores which are so important in certain parts of our own and other countries, and the data and conclusions set forth in the following pages are the outcome of experiments on telluride ores from Cripple Creek, Colorado. From them it will be seen that there is no occasion to question the substantial accuracy of the crucible method, as tested by careful determinations in the wet way. Incidentally the question of losses of gold in assaying, particularly during cupellation and parting, has been looked into, for concerning these points the most contradictory statements are to be found in the literature. Only after most of the work upon the ores had been completed was this fully impressed upon us and the extent of some of these losses duly appreciated. Had this appreciation come earlier we might have been able to offer still more satisfactory results for our assays.

PART I. ASSAY OF CRIPPLE CREEK TELLURIDE ORES.

Nature of the Ores Assayed.

Efforts were made to procure two ores of somewhat widely differing gold content and, with a view to the preparation of a homogeneous sample, containing as little free gold as possible. As received, through the kindness of Mr. W. M. Bainbridge, of the El Paso Consolidated Gold Mining Company, and of Dr. Waldemar Lindgren,

of the Geological Survey, the samples were marked 6 and 12 ounces per ton respectively, but they were actually much richer and of nearly equal value, approximately 15 and 19 ounces to the ton. At least 10 pounds of each was available. The ores were from a narrow fissure in granite, and were themselves practically granite, carrying pyrite in some quantity, the higher grade sample *b* more than *a*; some calcite; also traces of copper and molybdenum, as shown by determinations on 100 grms. Other constituents were not looked for. The tellurium also was quantitatively determined, in 50 grm. portions, in order to judge of the composition of the telluride mineral. As given below, silver is, no doubt, a trifle low, because of the impossibility of making exact allowance for loss in assaying.

TABLE I.—Amounts of certain Constituents of the Ores.

	<i>a</i> (per cent).	<i>b</i> (per cent).
Te	0.0742	0.092
Au	0.0506	0.060
Ag	0.0075	0.0103
Cu	0.0059	0.0070
Mo	0.0015	0.0018

Assuming none of the gold and silver to be free, but all in combination with tellurium, the following percentage compositions for the telluride have been calculated from the foregoing table:—

Calculated Composition of the Tellurides.

	<i>a.</i>		<i>b.</i>	
	Per cent.	Atomic ratio.	Per cent.	Atomic ratio.
Te ..	56.09	1.78	56.68	1.80
Au ..	38.24	1.00	36.97	1.00
Ag ..	5.67		6.35	
	100.00		100.00	

If the tellurium has been correctly determined, the above results indicate the probable presence of free gold, for from what we know of the occurrence of gold-silver tellurides at Cripple Creek they probably all conform to the general formula MTe_2 . That the telluride here present must then be largely if not wholly sylvanite, assuming absence of other silver minerals, is indicated by the amount of silver shown by the analyses, which is considerably in excess of that in even the richest known calaverite. It is not impossible that both calaverite and sylvanite as well as free gold are present. From the ratio of gold to silver in a second pair of samples, a_1 , and b_1 , which, as mentioned later, were taken from a lower position in the original sample bags, so that a considerable mechanical sorting had ensued since the bags were filled, the suspicion may be justified that the silver is in part a constituent of some mineral other than a telluride. For if the assays are correct there is a diminution in the silver as the gold increases, as shown by the following comparison:—

	<i>a</i> (ozs.).	<i>a</i> ₁ (ozs.).	<i>b</i> (ozs.).	<i>b</i> ₁ (ozs.).
Ag ..	2.19	2.07	3.00	2.87
Au ..	14.53	15.60	17.75	19.63

That not all the silver may thus be assigned elsewhere is, however, likely from the fact that the ratio of tellurium to gold alone is much in excess of 2 to 1. But too much weight must not be attached to the above values for silver, and therefore speculations of this sort are of little importance.

Preparation of the Samples.

Considerable portions from the tops of the bags containing the coarsely crushed samples received were ground fine enough to pass a sieve of 100 meshes to the linear inch and mixed for what was considered a sufficient time to insure homogeneity. The amounts thus prepared proved inadequate for the completion of the work, so other portions were ground fine enough to pass a sieve of 150 meshes and mixed more intimately even than in the first instance; this

* United States Geological Survey. Bulletin No. 253. (Series E, Chemistry and Physics, 44).

being done because the first results on sample *b* were somewhat less satisfactory and less accordant than those on *a*, a condition which it was hoped finer grinding would remedy. These second samples were found to be markedly richer in gold than the first, due doubtless to their having been taken from a greater depth in the original bags. They represented practically new ores, and, to simplify references, will be designated *a*₁ and *b*₁.

Combination Wet and Fire Assay.

Throughout the literature it is prescribed that for wet assay of gold ores they should be subjected to a preliminary roasting for the removal of sulphur chiefly. Since, however, it is pretty certain that there is loss of gold by volatilisation in the roasting of telluride ores, it seemed imperative to disregard these directions and to treat chemically the unroasted ore. No attempts were made to test different methods of attack and subsequent treatment because of lack of time. The method employed in all cases was the following:—

Fifty-grm. portions in duplicate were mixed with water in large porcelain basins, and strong nitric acid was added by degrees with constant stirring till action had nearly ceased. Then bromine water was added in excess to oxidise the gold and sulphur and precipitate the silver. No artificial heat was employed. The following morning the insoluble matter was collected on filters and washed ten times with water containing bromine and some hydrochloric acid, then two or three times with pure water.

It was found impossible to extract the whole of the gold by wet treatment. The residues always yielded by fire assay small amounts of gold, usually under 0.1 mg. when properly washed, besides nearly all the silver.

The combined filtrates were evaporated in the original porcelain basins to near dryness, then treated with hydrochloric acid and covered for a time. When action ceased the covers were removed and evaporation continued, hydrochloric acid being added two or three times more at proper intervals. When the residues were now digested with dilute hydrochloric acid and a little bromine water, to insure solution of the gold, there remained undissolved considerable calcium sulphate, which was collected on a suitable-sized filter and the filtrate received in a beaker. The first calcium sulphate residues thus obtained were found by fire assay to be free from gold, but all those obtained in subsequent tests were added to and assayed with the main residues.

The filtrates contained all the iron in an oxidised form and a slight excess of bromine. Without attempting to reduce the ferric iron to ferrous by sulphurous acid, whereby tellurium would have been in part precipitated as well as the gold, a large excess of filtered ferrous sulphate solution was added, which induced complete precipitation of the gold alone, without any tellurium. The completeness of precipitation was proved by the failure to detect any gold in the subsequently precipitated tellurium.

After twenty-four hours the precipitated gold was collected on a 9 c.m. paper filter of 0.00005 grm. ash content, carefully washed with cold water, then with warm dilute hydrochloric acid to extract iron from the paper, and finally with hot water. Paper and contents were burned in a clean porcelain crucible, and the contents most carefully transferred to the pan of the assay balance and weighed as nearly as might be to hundredths of a m. gm. As a check the gold was then generally cupelled with 3 or 4 grms. of pure lead in order to eliminate the error introduced by paper ash and any possible failure to wash the filter thoroughly. A companion cupellation with a similar amount of proof gold afforded the correction for gold loss during cupellation. A number of the beads thus obtained from the ore were collectively tested most carefully for silver, with negative results.

It was said above that it was not possible to extract quite all of the gold from the ore, and that the residues insoluble in acid were treated by fire assay in order to recover the

amount retained. The retention was probably owing to particles of telluride inclosed in gangue matter, or of gold in sulphur which had been separated but not fully oxidised by the treatment with nitric acid and bromine. These residues were assayed in crucibles with the following charge: Litharge, 2 A. T.; soda, 1 A. T.; borax, 10 grms.; argol, 2 grms.; salt, cover. The lead button thus obtained weighed about 20 grms. and yielded on cupellation nearly all the silver of the ore and a small amount of gold, which latter was obtained pure by direct parting. It was not deemed necessary to examine slags or cupels for their possible gold contents, owing to the minute amount in question, nor was any attempt made to determine by the wet way the exact amount of silver that the ore held.

TABLE II.—*Combination Wet and Fire Assays for Gold in Cripple Creek Ores.*

(Fifty grms. in each case).

Residues. M.grm.	By FeSO ₄ . M.grms.	Total.		After cupellation.	
		M.grms.	Ozs. per ton.	M.grms.	Ozs. per ton.
Sample <i>a</i> .					
0.08	25.29	25.37	14.80	—	—
0.04	25.22	25.26	14.73	25.22	14.71
0.08	25.73	25.85	15.08	25.42(<i>a</i>)	14.82
0.06	25.63	25.69	14.98	25.30(<i>a</i>)	14.76
Sample <i>a</i> ₁ .					
0.12	26.48	26.60	15.52	26.51	15.46
0.16	26.32	26.48	15.45	26.45	15.43
0.05	26.69	26.74	15.60	26.59	15.51
0.12	26.89	27.01	15.76	26.73	15.59
Sample <i>b</i> .					
0.13	—	—	—	—	—
0.12	29.56	29.68	17.32	29.45	17.18
0.07	30.84	30.91	18.03	30.57	17.83
0.12	30.50	30.62	17.86	30.17	17.60
Sample <i>b</i> ₁ .					
0.98	32.54	33.52	19.55	33.35	19.45
0.37	33.13	33.50	19.54	33.32	19.44
0.10	33.10	33.20	19.58(<i>b</i>)	33.07	19.49(<i>b</i>)
0.11	33.85	33.96		33.76	

(*a*) These beads contained a very little silver, which was lost in process of parting.

(*b*) The assays were made in pairs, and by accident a part of the washings of one assay was evaporated in the wrong dish. The assays were run through separately, but only the mean is taken for final comparison.

There is seen to be a very fair agreement in each of the several series except *b*, an exception which was apparent also in the fire assay tests of the ore. It was largely for this reason that fresh samples of each ore were prepared (*a*₁ and *b*₁), as before mentioned.

(To be continued).

Educational Post Cards.—The Country Press, of 19, Ball Street, Kensington, W., are issuing a novel series of Educational Post Cards, the first example of which (Natural History Department) is a picture presentment, on seven cards, for the price of sixpence, of the whole of the British Ferns (42 species, nature prints) from the illustrative plates of Mr. Francis George Heath's work, "The Fern Paradise." These are to be followed by other representations on post cards of natural history subjects and others likely to have an educational value.

CONDENSATION COMPOUNDS OF CAMPHOR-
OXALIC ACID AND AMINES.*SEVENTH COMMUNICATION ON CAMPHOROXALIC
DERIVATIVES.By J. BISHOP TINGLE, Ph.D., F.C.S.,
and
WILLIAM EDWIN HOFFMAN, Jun., Ph.D.

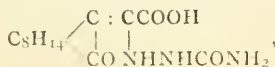
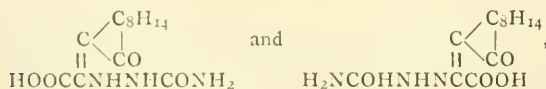
(Continued from p. 88).

ACTION OF AMINES ON CAMPHOROXALIC ACID (continued).

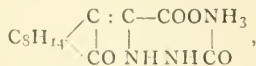
XI. 1,2,4-Nitrotoluidine.

When nitrotoluidine ($\text{CH}_3 = 1$, $\text{NH}_2 = 2$, $\text{NO}_2 = 4$) is heated at 150° with camphoroxalic acid in alcoholic solution under pressure for several hours, *nitrotolylcamphorformeneamine*,—is obtained. It crystallises readily from alcohol in minute bright yellow needles which melt at 192° . It was not possible to isolate the corresponding carboxylic acid or salt, although a number of experiments under varying conditions were made with this object.

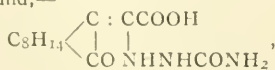
XII. Semicarbazine.

When semicarbazine and camphoroxalic acid react in the presence of acetic acid, a compound is formed with the composition of *semicarbazine camphorformeneaminecarboxylic acid*,—It crystallises from alcohol in stout colourless prisms melting at 200° . When dissolved in boiling glacial acetic acid, crystals were deposited in the form of clusters of fine needles which melt at $209\text{--}210^\circ$. If the compound obtained from glacial acetic acid is dissolved in sodium carbonate and re-precipitated by acid, a gelatinous substance is formed, which crystallises from acetone in slender colourless needles melting at the same temperature as before, viz., $209\text{--}210^\circ$. These two substances have the same empirical formula and maintain their distinctive melting-points even after heating for some time at 110° . They dissolve readily in sodium-hydrogen carbonate, and are re-precipitated by acids in the form of a jelly. With alcoholic ferric chloride, no colour reaction is produced in either case. All these facts lead to one of two conclusions: either the compounds are stereoisomers of the maleic-fumaric type,—

or there is the formation of an inner salt,—

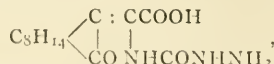


which is changed by the glacial acetic acid into the open-chain compound,—



In the case of these semicarbazine derivatives we have represented the condensation as having taken place between the hydrazine nucleus and the camphoroxalic acid. Although this is in accordance with precedent, it may well

be that in one or both compounds it is the carbamide group which has reacted, giving—



and its stereoisomer. Further work will be necessary to decide between these various possibilities; the subject is being more fully investigated in the laboratory of the Johns Hopkins University.

XIII. Orthophenylenediamine.

When orthophenylenediamine and camphoroxalic acid are allowed to react in alcoholic solution at the ordinary temperature, there is formed the camphoquininoxaline compound, which was prepared by J. Bishop Tingle by the action of sodium camphoroxalate, and also of ethylcamphoroxalate, on orthophenylenediamine. It crystallises from alcohol in bright yellow needles which melt at 246° . The formation of this camphoquininoxaline by the interaction of sodium camphoroxalate, ethyl camphoroxalate, or camphoroxalic acid respectively, is somewhat remarkable, as it shows the tendency of such a phenylenediamine derivative, in which the amino-groups are in the ortho-position, to form a five-membered ring compound even under conditions where we should not expect such an action to take place.*Paraphenylenediamine* was treated with camphoroxalic acid under the same conditions as were used for the ortho-compound, and also under others, in the hope that it might react and throw some light on this question of ring formation, but no definite product could be obtained.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 15th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MESSRS. H. B. Hartley and H. L. Tidy were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Richard Henry Beckett, B.Sc., Inval, Haslemere, Surrey; Herbert Reginald Cooper, Redington, Northwood, R.S.O.; Charles Davidson, 37, Herriot Street, Pollok-shields, Glasgow; Edward Gardner, 70, Parliament Hill Mansions, Highgate Road, N.W.; Richard Godfrey Hamilton Garvey, 25, Park Mansions, Battersea; William Tabor Lattey, Corpus Christi College, Cambridge; Hamilton McCombie, M.A., B.Sc., Ph.D., The University, Birmingham; Thomas Jenkins Murray, Ph.D., The University, Birmingham; Edgar Gall Oliver, M.A., Chigwell School, Essex; Lawrence George Richardson, 14, Ashgrove, Horton, Bradford; David Somerville, B.A., M.D., 31, Manor House, Marylebone; Foster Sproxtón, B.Sc., Uplands, Alexandra Park Road, Wood Green, N.; Harold Augustine Tempamy, B.Sc., St. Johns, Antigua, B.W.I.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As *Vice-Presidents*—Prof. W. H. Perkin, jun., F.R.S., and Dr. Rudolph Messel, vice Prof. W. R. Dunstan, F.R.S., and Mr. D. Howard.As *Ordinary Members of Council*—Prof. W. Gowland, Dr. H. A. D. Jowett, Dr. F. E. Matthews, and Prof. A. G. Perkin, F.R.S., vice Prof. A. E. Dixon, Prof. J. J. Dobbie, F.R.S., Dr. E. J. Mills, F.R.S., and Prof. J. M. Thomson, F.R.S.

Mr. E. Grant Hooper, Dr. H. F. Morley, and Dr. H. R. Le Sueur were elected Auditors to audit the Society's accounts.

* From the *American Chemical Journal*, xxxiv., No. 3.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—George Ernest Banner; Arthur Ernest Barker, B.A., B.Sc.; William Edward Bell; Charles Frederick Polwhele Blatchley, B.A.; Thos. Going Stoney Bogue; Arthur Forbes Braid; Richard Victor Briggs; William Caldwell, M.A.; Reginald William Lane Clarke; Wm. Boulton Conyngham; Stephen Lewis Courtauld, B.A.; Thomas Harold Durrans; Frederick Watkins Evans; Hans Eduard Fierz, Ph.D.; Walter Hamis Glover, Ph.D.; Harry Sands Grindley, D.Sc.; William Prince Hayworth; Henry Carlyle Irving, B.A.; Llewellyn Thomas Jones, B.Sc.; William Henry Matthews Jones; Robert Le Rossignol, B.Sc.; John McDowall; William Mace; George Frederick Wesley Martin; Samuel Parfitt; John Parkin, M.A.; William Hughes Perkins, B.Sc.; John Edmund Pitman, B.Sc.; Harold Rogerson, M.Sc.; Philip Foale Rowsell; John Kirby Shrimpton; Frank Smith, B.Sc.; George Stanley Talbot; Percy Charles Thornton; Arthur William Thorp; Ronald William Tonkin; Franklin Wilfred Walker; Richard Alfred Warren; Hardolph Wastenays; Henry Edgar Watt, M.Sc.; Elkan Wechsler, Ph.D.; Harold Joseph Wheaton; Herbert William Mills Willett; Richard Willstaetter, Ph.D.; Ernest Edwin Wolfe; John William Yates, B.Sc.

Of the following papers, those marked * were read:—

*35. "Cuprous Formate." By ANDREA ANGEL.

The compound described as cuprous formate by Joannis (*Abstr.*, 1904, i., 644), having the formula $(\text{HCO}_2)_2\text{Cu}_2 \cdot 4\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, should be named ammonio-cuprous formate, since it is quite different in properties from the substance prepared by dissolving cuprous oxide in an aqueous ammoniacal solution of ammonium formate under petroleum, diluting the solution with alcohol, and acidifying with formic acid, when crystals are deposited which are collected in an atmosphere of hydrogen and washed with ethyl formate. Cuprous Formate, $(\text{HCO}_2)_2\text{Cu}_2$, consists of colourless crystals which are very easily decomposed; water immediately hydrolyses the substance to cuprous oxide and formic acid, sodium carbonate solution decomposes it with effervescence, ammonia solution decomposes it with a slight hissing noise, and dilute sulphuric acid at once produces a precipitate of metallic copper. Dilute formic acid acts similarly, although more slowly. Moist air rapidly hydrolyses it, turning it orange-red, but in a desiccator over sulphuric acid it may be preserved apparently for an indefinite time. Owing to the ease with which the substance is decomposed, the preparation requires special precautions in regard to the strength of the solutions employed. The method of preparation may be employed, with modifications, for the production of other cuprous salts.

DISCUSSION.

Mr. A. VERNON HARCOURT said that Mr. Angel's research arose out of some experiments on the gradual heating of cupric acetate in a vacuum, an account of which had already appeared in the *Transactions*.

Both cupric acetate and cupric formate when strongly heated in a glass vessel deposit a mirror of copper on the glass, showing that a gas containing copper has been formed. The temperature of decomposition of cuprous acetate is very near its temperature of volatilisation, and neither it nor cuprous formate can be obtained, except in very small proportion, by sublimation from the cupric salt.

*36. "The Solubility of Triphenylmethane in Organic Liquids, with which it Forms Crystalline Compounds." By HAROLD HARTLEY and NOEL GARROD THOMAS.

Experiments were made on the crystallisation of triphenylmethane from a large number of organic liquids in order to see in what cases a crystalline compound is formed with the solvent. From benzene, thiophen, pyrrole, and aniline solutions, it crystallises under certain conditions with one molecule of the solvent, and a microscopic study of crystals of the four compounds has shown that they all

belong to the rhombohedral system, forming an isomorphous series.

The solubility of triphenylmethane in each of the four liquids and also in pyridine has been determined by a modification of the method devised by Kuriloff. Weighed quantities of solvent and solute are sealed in small glass tubes, and these are placed in a water-bath. By varying the temperature of the bath, two temperatures can be determined, at the lower of which the last crystal left undissolved is growing, and at the upper the same crystal is dissolving. These temperatures are usually 0.4° to 0.5° apart, and their mean has been taken as the temperature of saturation.

Experiments were also made on the spontaneous crystallisation of supersaturated solutions of triphenylmethane in each of the foregoing solvents by cooling solutions in sealed tubes after they had been heated sufficiently to destroy all crystalline nuclei. When the tubes were shaken during the cooling, crystallisation took place at definite temperatures. The results confirm the existence of a metastable region in which supersaturated solutions cannot crystallise spontaneously. The limit of this region where the solutions pass into the labile state and crystallise can be represented by a curve, for which Miers and Isaac have suggested the name "supersolubility curve." It runs approximately parallel to the solubility curve at a distance from it depending on the respective solvent and solute.

*37. "The Spontaneous Crystallisation of Supersaturated Solutions." By HAROLD HARTLEY.

The author discussed the different views of Ostwald and de Coppet on this subject in view of the experiments described in the preceding communication, and those of Miers and Isaac (*Proc.*, 1906, xxii., 9). It was shown how the difference between metastable and labile solutions might be explained from the kinetic standpoint as a result of the increased solubility of the small crystals which must be first formed in a spontaneous crystallisation.

DISCUSSION.

Prof. MIERS welcomed these investigations as new examples of the importance of the supersolubility curve, and called attention to the fact that the authors could not have established their results without a practical knowledge of crystallography.

Sir WILLIAM RAMSAY pointed out the analogy between the behaviour of crystallisable solution in the metastable and stable states with that of a super-heated liquid, and suggested that Mr. Hartley might derive some help by a study of such behaviour.

Mr. HARTLEY, in reply, said that small crystals besides being abnormally soluble must also have a lower melting-point than larger individuals, and that this fact would explain the usual occurrence of superfusion. Mr. P. W. Robertson and he were just starting to investigate the conditions under which a number of pure organic substances crystallise spontaneously, and the former had suggested that the variation of melting-point with the size of a crystal might explain some of the irregularities which had been observed in cryoscopic work with such solvents as thymol. Supersaturated solutions did not crystallise immediately on reaching the labile state unless they were vigorously shaken; thus the pull on the solution, which was suggested by Sir William Ramsay's analogy of the continuous isothermal as necessary to start crystallisation, was actually realised in the continuous production of fresh liquid surfaces.

*38. "Preparation and Properties of some New Tropeines." By HOOPER ALBERT DICKINSON JOWETT and ARCHIE CECIL OSBORN HANN.

The object of this investigation was primarily to determine whether any difference in physiological action could be observed between tropeines containing a lactone grouping and their corresponding hydroxy-acid, similar to that recorded in the case of pilocarpine and pilocarpic acid (Marshall, *Journ. Physiol.*, 1904, xxxi., 153). For this purpose, the tropeines of methylparaconic, terebic, and phthalidecarboxylic acids were prepared, when it was

found that both terebyl- and phthalidecarboxyl-tropeines, which produce an atropine-like effect on the heart, lose this action after a molecular proportion of alkali has been added to the base, thus showing in aqueous and alkaline solution a difference in action analogous to that observed in the case of pilocarpine.

In addition to the tropeines already mentioned, the glycollyl- and protocatechyl-derivatives were prepared and the opportunity taken to test Ladenburg's generalisation. According to this chemist, a tropeine, in order to possess mydriatic action, must contain a benzene nucleus and a fatty hydroxyl attached to the same carbon atom as that bearing the carboxyl group. It was found that this did not strictly hold, as terebyltropeine possessed a distinct mydriatic action. It would appear, however, that the conditions most favourable for the development of the mydriatic action in a tropeine are those stated by Ladenburg, namely, that the acyl group should contain a benzene nucleus and an aliphatic hydroxyl in the side-chain containing the carboxyl group.

*39. "Studies in Asymmetric Synthesis. IV. The Application of Grignard's Reaction for Asymmetric Syntheses." By ALEXANDER MCKENZIE.

The author has studied the action of magnesium propyl iodide, magnesium isobutyl iodide, and magnesium α -naphthyl bromide respectively on *l*-menthyl benzoylformate, and effected in each case an asymmetric synthesis of a substituted *l*-glycollic acid. The influence of the *l*-bornyl as contrasted with that of the *l*-menthyl grouping was examined by acting on *l*-bornyl benzoylformate with various magnesium alkyl halides; the effect of the *l*-bornyl grouping was to diminish the levorotation of the mixture of substituted glycollic acids obtained; thus, whilst the mixture of *d*- and *l*-atrolactic acids obtained from *l*-menthyl benzoylformate and magnesium methyl iodide had $[\alpha]_D -9.5^\circ$ in ethyl-alcoholic solution, the mixture from *l*-bornyl benzoylformate under similar conditions gave $[\alpha]_D -1.9^\circ$.

A mixture of *d*- and *l*-phenylisobutylglycollic acids containing an excess of the *d*-acid was produced from *l*-bornyl benzoylformate and magnesium isobutyl iodide, whereas the mixture was levorotatory when *l*-menthyl benzoylformate was used. Similarly, a dextrorotatory mixture of acids was produced by the action of *l*-bornyl benzoylformate on magnesium α -naphthyl bromide.

The asymmetric synthesis of *d*-atrolactic acid was produced by the action of magnesium phenyl bromide on *l*-menthyl pyruvate.

When *l*-menthyl acetoacetate, *l*-menthyl ethylacetoacetate, or *l*-menthyl diethylacetoacetate is submitted to the Grignard reaction, no asymmetric synthesis occurs, the first of these substances reacting in accordance with its enolic structure. A slight asymmetric synthesis was, however, detected when *l*-menthyl lavulate was used.

40. "o-Cyanobenzenesulphonic Acid and its Derivatives." By A. JAMIESON WALKER and ELIZABETH SMITH.

Reference was made to the work of Jesurun (*Ber.*, 1893, xxvi., 2288) on *o*-cyanobenzenesulphonic chloride, and to that of Remsen and others (*Am. Chem. Journ.*, 1895, xvii., 309 and 347; *Ibid.*, 1896, xviii., 794 and 819), and List and Stein (*Ber.*, 1898, xxxi., 1648) on ammonium *o*-cyanobenzenesulphonate.

The authors then described a modification of Jesurun's method for the preparation of *o*-cyanobenzenesulphonic chloride and the isolation from the mother-liquor of *o*-cyanobenzenesulphonic acid, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, which crystallises from water in white needles melting at $279-279.5^\circ$. Its silver salt has been prepared, and the action of nitric acid and bromine on the acid investigated.

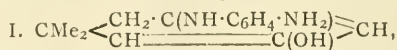
Reduction of the chloride with zinc dust yields *o*-cyanobenzenesulphonic acid, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{H}$, which crystallises in small white needles melting at $226.5-228^\circ$. With bromine, this acid yields two compounds melting at $156-156.5^\circ$ and $172.5-173^\circ$ respectively, but containing no bromine. Their constitution is still being investigated. Nitrous acid converts the sulphonic acid into a yellow

solid, probably *o*-cyanodibenzsulphohydroxamic acid, $\text{N}[(\text{C}_6\text{H}_4(\text{CN})\cdot\text{SO}_2)_2]\cdot\text{OH}$.

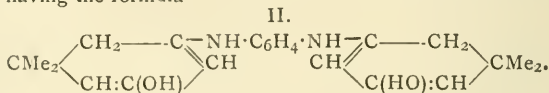
Heating with dilute caustic soda and subsequent acidification transform the chloride into a substance (m. p. $221.5-223^\circ$) with the sweet taste of "saccharin," and not into the sulphonic acid.

41. "The Condensation of Dimethyldihydroresorcin and of Chloroketodimethyltetrahydrobenzene with Primary Amines. Part II. Diamines; *m*- and *p*-Phenylenediamines." By PAUL HAAS.

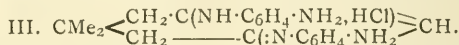
Dimethyldihydroresorcin condenses, in alcoholic solution, with one molecular proportion of a diamine, giving an 80 per cent yield of the compound—



together with a small amount of a disubstituted amine having the formula—



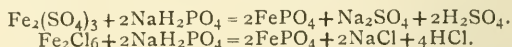
A better yield of the latter substance is obtained by prolonged boiling in alcoholic solution of one molecular proportion of the Compound I, with a second molecule of dimethyldihydroresorcin. Chloroketodimethyltetrahydrobenzene condenses with two molecules of a primary diamine to give a hydrochloride having the following formula:—



The corresponding base is strongly alkaline to litmus, whereas the Compound I, has a neutral reaction; it cannot be made to condense further with dimethyldihydroresorcin, as, owing to its strongly basic nature, it is precipitated by this substance from an alcoholic solution in the form of an insoluble resorcin salt having the formula $\text{C}_{20}\text{H}_{24}\text{N}_4\cdot\text{C}_8\text{H}_{12}\text{O}_2$.

42. "A Modification of the Volumetric Estimation of Free Acid in the presence of Iron Salts." By C. CHESTER AHLUM.

Because of the inapplicability of indicators in the titration of free acid in the presence of iron salts, the author devised a modification in which the iron is removed from solution, making a titration possible. The iron is precipitated by means of sodium dihydrogen phosphate. The iron phosphates are filtered off, and the filtrate titrated with standard sodium hydroxide. In the reaction of the ferric salt with the sodium dihydrogen phosphate, a definite quantity of acid is liberated, necessitating a correction in the amount of acid found in the titration.



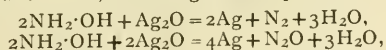
The amount of acid is directly proportional to the amount of ferric iron present, the latter being estimated previous to the titration. The difference between the amount of acid found in the titration and the amount of acid equivalent to the ferric iron present gives the true amount of free acid. A table giving the results of a number of estimations of free acid in mixtures of known quantities of ferric sulphate and sulphuric acid shows a considerable degree of accuracy.

Calcium, magnesium, and ferrous salts do not interfere with the estimation, and the method is applied to the analysis of natural waters containing iron salts and free acid.

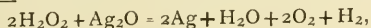
43. "The Theory of Alkaline Development, with Notes on the Affinities of certain Reducing Agents." By SAMUEL EDWARD SHEPPARD.

The author first dealt with the reactions of hydroxylamine and hydrogen peroxide respectively with silver salts, with notes on the reactions of organic reducers. It was shown that at moderate concentrations one molecule of

hydroxylamine reduces one molecule of silver salt, but at great dilutions two, according to the equations:—



whilst one molecule of hydrogen peroxide reduced one molecule of silver salt, probably according to the equation—



hydrogen being one of the reaction products. The bearing on the molecular condition in solution of these substances was discussed. With organic reducers, such as polyphenols and aminophenols, a peculiar case of "coupled" reaction was examined, wherein the mutual presence of organic compound and sulphite retarded the total oxidation. The author has also investigated the dynamics of development with these reducers.

44. "*Resolution of 2 : 3-Dihydro-3-methylindene-2-carboxylic Acid into its Optically Active Isomerides.*" By ALLEN NEVILLE.

When ethyl benzylacetoacetate is treated with concentrated sulphuric acid, 3-methylindene-2-carboxylic acid is formed, which on reduction with sodium amalgam gives 2 : 3-dihydro-3-methylindene-2-carboxylic acid. This acid forms with *l*-menthylamine a well-defined crystalline salt, which on crystallisation from ethyl acetate gives, after a few crystallisations, the pure salts of the *d*-acid and *l*-base. This substance crystallises in long white needles, melts at 170°, is easily soluble in all the ordinary organic media except ethyl acetate and ether, and has $[\alpha]_D + 27.35^\circ$ and $[\text{M}]_D + 89.63^\circ$. On decomposing this salt, *d*-2 : 3-dihydro-3-methylindene-2-carboxylic acid was obtained, which crystallised in long flat needles melting at 86°. It was insoluble in water, but soluble in all the ordinary organic media; it gave in alcohol $[\alpha]_D + 67.28^\circ$ and $[\text{M}]_D + 118.41^\circ$, and in benzene $[\alpha]_D + 76.86^\circ$ and $[\text{M}]_D + 135.27^\circ$. The sodium, potassium, barium, silver, and lead salts and the methyl ester were prepared.

From the more readily soluble portions of the menthylamine salt, the levorotatory acid was isolated. This was exactly similar in specific rotation and other properties to the corresponding dextrorotatory isomeride.

NOTICES OF BOOKS.

A Manual of Pharmacology. By WALTER E. DIXON, M.A., Cantab., M.D., B.S., B.Sc. Lond., D.P.H. Camb., &c. London: Edward Arnold. 1906.

THE plan adopted by the author of this work is excellent, and its use will do much to lighten the labours of the medical student by lessening the tedious memory work, which has hitherto been a stumbling block to many. The book gives a full general account of pharmacology, assuming that the reader possesses a fair working knowledge of physiology and chemistry. The drugs are classified on a basis partly chemical and partly physiological, and the source and chemistry of each drug is briefly discussed, while its action and effects are fully described and illustrated; notes are also added on the pharmacopœial preparations, doses, &c. Only a very small amount of therapeutics is introduced, and that merely to illustrate various points in pharmacology. The manual is thoroughly satisfactory in every respect, and deserves to be widely used by medical students and practitioners.

Einführung in die Thermodynamik auf energetischer Grundlage. ("Introduction to Thermodynamics based upon Energetics"). By Dr. JULIUS MEYER. Halle-a-S.: William Knapp. 1905.

In this work the theory and results of thermodynamics, or rather such results as are of practical importance, for the book makes no attempt to cover the whole ground of the

science, are clearly and simply explained; the discussion of energy, which is represented as a reality and not an abstract conception, being particularly satisfactory. A short mathematical introduction gives a sketch of the meaning and use of differential coefficients and of integration, sufficient at any rate for a clear understanding of the earlier parts of the book, although the student might find it desirable to supplement the knowledge he acquired from the book with the help of some treatise on the calculi, in order to profit fully by such mathematical analysis as introduced in the later sections. We can recommend this book for the use of chemists to pave the way for the more difficult text-books in thermodynamics; especially in the earlier parts it describes methods and results in clear language, and very full explanations are given wherever difficulties are likely to occur to the beginner.

Etude Générale des Sels. ("General Study of Salts"). By ALFRED DITTE. Vol. I. and II. Paris: H. Dunod and E. Pinat. 1906.

THESE two volumes contain an exhaustive account of our knowledge of the subject of salts, special stress being laid upon defining and comparing the properties of groups rather than of individual members of each group. Vol. I. deals with the Binary Salts, and gives full details as to their preparation, chemical and physical properties, and the action of heat and electricity upon them, while copious tables are given of heats and formation, the author believing in the importance of emphasizing thermo-chemical facts. The second volume deals with the oxygenated Ternary Salts, and opens with a discussion of their general properties, and the action of various chemical reagents upon them; in the chapter on the action of water upon salts the theory of ionisation in dilute solutions is briefly considered, while the chapter on the reciprocal actions of acids, bases, and salts, and that on the action of acids upon salts, contain much interesting theoretical matter, clearly written and well arranged. In the last part of the volume the general principles are applied to the various groups of ternary salts. The book is one which a student will do well to consult for those important generalisations which are of such great value in showing him how to find his way along the paths in the forest of inorganic chemistry, as Prof. Ostwald puts it, while all the theoretical parts of the book are characterised by lucidity and admirable judgment, and the reader will find that he has nothing to unlearn when he passes on to the study of higher treatises.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

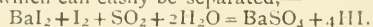
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 5, January 29, 1906.

New Researches on Insoluble Alkaline Compounds contained in Living Vegetables.—M. Berthelot.—The existence of insoluble potassium compounds and those of other alkaline metals in dead leaves, &c., and their derivatives, is of great interest, on account of the changes and migrations of this class of compound at different periods of vegetation and in the different organs of the plant. The author, in the present paper, describes a series of experiments executed on an oak tree.

Sulphates of the Rare Earths.—Camille Matignon.—The author prepares anhydrous sulphates of lanthanum, praseodymium, neodymium, and samarium. He starts with precipitated oxalates, which are carefully calcined at 800°. The oxide thus prepared is mixed with a slight excess of sulphuric acid, and the whole brought to a dull

red heat. Having prepared the pure anhydrous sulphates, the author finds the heat of solution. He also finds the heats of solution of the oxide in sulphuric acid. He concludes from the results obtained that the oxides of the rare earths from the point of view of their basic function are intermediate between the alkaline earth oxides and those of magnesium.

Rapid Preparation of Solutions of Hydriodic Acid.—F. Bodroux.—In ordinary, to prepare solutions of hydriodic acid with great rapidity a certain weight of iodine is divided into two equal parts. The first is treated with barium dioxide in presence of water, and is transformed into barium iodide, $\text{BaO}_2 + \text{I}_2 = \text{BaI}_2 + \text{O}_2$. The second portion of iodine is dissolved in the liquid thus obtained. A current of sulphurous anhydride is then allowed to pass through the liquid until decoloration just takes place. Hydriodic acid and barium sulphate are formed, which can easily be separated,—



An Alloy of Thorium and Aluminium.—O. Hönlischmid.—The reduction of thorium oxide by means of silicon in the electric furnace, as well as the direct combination of the silicide and thorium in presence of aluminium in a vacuum at 1000°, and finally the reduction of a mixture of potassium fluosilicate and the double fluoride of thorium and potassium by means of aluminium, are a means of preparing a crystalline thorium silicide in quadratic plates. These crystals very much resemble pure graphite, and have a composition corresponding to the formula ThSi_2 . Under analogous conditions the reduction of thorium oxide by means of aluminium in the electric furnace, the direct combination of aluminium and thorium in a vacuum, as well as the reduction of the double fluoride of potassium and thorium by means of aluminium, allow of the preparation of an alloy of thorium and aluminium crystallising in long hexagonal prismatic needles, with colour and metallic lustre resembling aluminium, and having a composition corresponding to the formula ThAl_3 .

Researches on the Halogen Compounds of Barium and Strontium Borates.—L. Ouvrard.—The borates of barium and strontium seem to enter into combination with chlorine and bromine less easily than the corresponding calcium salt. In both the former cases the author has only succeeded in obtaining a single halogen compound. In the case of the alkaline earth iodides the very slight stability seems to prohibit them entering into combination with the borates of the same metals, at least under the conditions of the author's experiments.

α - and β -Campholytic Alcohols.—G. Blanc.—The present research completes the list of compounds which the author has been obtaining for several years past by the reduction of β -campholytic ether under different conditions. He now prepares:—(1) β -campholytic alcohol by the reduction of the ether by means of sodium in aqueous medium; (2) β -dihydrocampholytic alcohol by the reduction of the ether by means of sodium and alcohol with a yield of 60 per cent; (3) α -campholytic alcohol either by the reduction of the ether or by the reduction of the amide by sodium and alcohol.

MEETINGS FOR THE WEEK.

- MONDAY, 5th.—Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. "Ignition of Nitro-compound Explosives in Small Arm Cartridges," by W. D. Borland.
- TUESDAY 6th.—Royal Institution, 5. "Food and Nutrition," by Prof. William Stirling, M.D., &c.
— Society of Arts, 4.30. "Imperial Questions in the West Indies," by Sir Neville Lubbock, K.C.M.G.
- WEDNESDAY, 7th.—Society of Arts, 8. "The Artistic in Painting and Photography," by J. C. Dollman.
— Society of Public Analysts, 8. "Simple and Rapid Method for the Approximate Estimation of Boric Acid," by C. H. Cribb and F. W. F. Aroud. "Analysis of a Sample of Air extinguishing a Flame," by B. Blount. "Detection of Coconut Oil in Butter," by A. W. Thorp. "Composition of Milk," by H. Droop Richmond.

- THURSDAY, 8th.—Royal Institution, 5. "The Physiology of Plants," by Francis Darwin, M.A., &c.
FRIDAY, 9th.—Royal Institution, 9. "Some Dietetic Problems," by Robert Hutchison, M.D., &c.
— Physical, 8. "Velocities of the Ions of Alkali Salt Vapours at High Temperatures," by Prof. H. A. Wilson. "Some Experiments on Earth-currents at Kew Observatory," by Dr. Harker.
- SATURDAY, 10th.—Royal Institution, 3. "The Corpuscular Theory of Matter," by Prof. J. J. Thomson, F.R.S., &c.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Nitro-starch—Can any reader supply information relating to the recent bibliography of Nitro-starch?—J. W. G.

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THE CHEMICAL NEWS.

VOL. XCIII., No. 2415.

ON THE ESTIMATION OF INDUSTRIAL TARTARIC ACID.

By Dr. P. CARLES.

A MERCHANT has made the following experiment: Wishing to buy a large quantity of tartaric matters "mixtes" (by this word we mean the compound of tartrate of lime and bitartrate of potash) he has taken a sample on the lot with the precaution required in such a case, and that sample he has divided into six similar small ones, numbered from one to six. Two have been sent to Mr. X., an Italian chemist, specialist for tartaric matters, two others to Mr. Y., a French chemist, specialist in the same line, and the last two to Mr. Z., another French chemist, also a specialist.

Each of the three, ignorant of the similitude of the two parcels, gave the same figures for the two samples he analysed, which constitutes a good mark for all. But between X. and Y. there was a difference of nearly 2°, between Y. and Z. almost the same, so that between X. and Y.'s figures the difference was nearly 4°.

Persons knowing the market value of those matters will certainly be moved in reading the above results, and still more when they come to think of the large quantity of goods involved.

What can be the causes of all three chemists being at variance? To ascertain them we will successively examine the operations most aleatory of the Goldenberg and Geromon 1898 method. That method had been prescribed to the three experts.

Chlorhydric Acid.—Differences in density in the acid used are of small importance in this case, for the tartrates in a very fine powder are easily soluble in the acid, especially when diluted.

Gauging.—The author of this method has been careful to recommend to ascertain that the 50 c.c. measure is really half of the 100 c.c. one, volume given to the chlorhydric solution. It is most probable that nobody forgets that verification.

Transformation of the Tartrate of Lime into Neutral Tartrate of Potash.—This is, in our opinion, one of the points on which it is easiest to make a mistake. When, as is usually done, one pours the carbonate of potash into the chlorhydric liquor, a precipitation of the lime salts very often takes place, and that precipitation is the more rapid and abundant as the tartrate of lime occupies more room in the mixture. Now, although at our instigation Mr. Goldenberg has recommended in 1889 to be sure that the liquid remains alkaline until the end, nothing indicates with precision, after ten minutes ebullition, that the conversion of the tartrate of lime into potassic tartrate is complete. That is why, when the raw material is rich in tartrate of lime, if the washed precipitate is placed in contact with acetic acid, one sees that one part of it does not dissolve, and that it is tartrate of lime.

It is to obviate that state of things that we have proposed to pour, not the carbonate of potash into the chlorhydric solution, but to do the reverse, slowly and *à froid*, boiling afterwards the mixture for twenty-five minutes instead of ten. That modification offers the following advantages:—

1. With the first drops of acid liquor the carbonate of potash is transformed into bicarbonate.
2. This bicarbonate does not precipitate the salts of lime, for when the last drops of acid are poured all is invariably in dissolution.

3. When warming this liquid, without ceasing to agitate with the hand, the bicarbonates dissociate, the carbonic gas disengages itself with the speed that one wishes; and of the salts of lime separated by ebullition not one particle escapes the action of the carbonate alkaline.
4. Those particles are so small that the ebullition takes place quietly until the end and without any of those disquieting jumps which occur when one proceeds as said further above.
5. The conversion of tartrate of lime is complete, as everyone can verify in the way already described.

Transformation of the Bitartrate.—The separation of the neutral tartrate of potash, the washings, the evaporation to a nicety of the liquor and the transformation of the tartrate neuter into bitartrate by acetic acid carry no serious cause of error.

Washing of the Bitartrate.—Some make, by dilution in the capsule itself, the ten or twelve washings with alcohol necessary to extract the adhering acetic acid, and only at the end do they pass the precipitate through the conical paper. Others prefer to do all the washings on the filter itself by "lixiviation." We have always considered the first method as the better, because when the matter is gummy or "pectineuse," the alcohol passes without penetrating to the centre of the cone, which retains then its acetic acid.

Dissolution of the Bitartrate.—The author advises to pass it into a glass or conical vase and to dissolve it with the warm water used in rinsing the capsule. But it seems to us more prudent to replace it in the capsule, where the alkaline reaction of the glass is not to be feared, unless those glasses have been boiled a long time with chlorhydric water, a prudent method when they are to be kept specially for tartaric experiments.

Titrated Alkaline Solution.—Everybody agrees it should only be formed of soda free from carbonate, but one should not forget that, to our instigation again, Mr. Goldenberg has recommended to standardise it, to use bitartrate pure and not oxalic or sulphuric acid themselves standardised with care, such as was generally done scarcely fifteen years ago.

Standard Pure Bitartrate of Potash.—We affirm that it is not as easy as is commonly thought to obtain a salt worthy of that name, and yet its purity is here of capital importance. Some pretend to arrive at it by putting some cream of tartar (ground to a fine powder) to digest in some chlorhydric water, and by washing afterwards in distilled water. But we humbly confess that after using 500 of chlorhydric water at one-tenth to purify 400 of cream of tartar rich, and washing afterwards with 2 litres of water, we have only obtained, in spite of a loss of 20 per cent, a bitartrate at 99.35 per cent. We therefore believe absolutely necessary to prepare that standard bitartrate by synthesis as follows:—

In a litre of distilled water, dissolve when warm 100 of tartaric acid, filter, and divide into two equal parts. In one of them, boiling, add a solution made when cold of carbonate of potash pure in distilled water, and filtered until cessation of effervescence. Then add the tartaric acid kept in reserve slowly and without ceasing to stir with a glass spatula. Leave to cool, decant, and wash the deposit with warm distilled water. The product desiccated is pure, but is hygroscopic. Re-dissolve it in boiling distilled water, and decant the solution into other porcelain capsules. Next day separate the *eaux mères*, wash with distilled water, drain, and dry until constant weight in a water-bath.

You have then a perfectly reliable standard worthy of confidence to titrate the "sodique" liquor.

Test-tubes.—We have long ago said, with others, how unreliable are the instruments sold by the trade. The test-tubes are among that number. It is indispensable to always reserve the same. 1° to titrate the sodique liquor, 2° to titrate the bitartrate separated from the Goldenberg.

When one comes to think of the differences produced on the value of a waggon of goods by a few tenths of degrees of that instrument, one finds that the precaution is worth taking.

Indications.—Goldenberg advises the use of turnsol paper; others think that phenolphthalein indicates with more accuracy the limit of saturation. We are among these, but with one absolute condition, as with in fact all witnesses, that one operates with the bitartrate unknown in the same manner as with the standard pure bitartrate; using as much as possible the same weights of matter, an equal volume of water at the same temperature, and an equal number of drops of the indicator.

Such are the observations that we have noted during a long practice of this method of dosing the tartaric acid in the tartaric matters on the market. That method, saving a few exceptions, gives, without a doubt, perfect results. But the details given above tell clearly how necessary it is to have practiced it long, for as you have just read, the method admits of causes of errors both ways.

THE DISSOLUTION OF PLATINUM BY SULPHURIC ACID.

By MARCEL DELÉPINE.

If we consult text-books, papers, or dictionaries of chemistry as to the action of sulphuric acid with regard to platinum, it becomes very difficult to form an opinion. Of twenty-one French and German works, of which the oldest dated back only to 1880, five stated that platinum is attacked slightly or slowly by sulphuric acid when heated, seven that it is not attacked, and nine that it is only attacked by a nitrous sulphuric acid. These divergent opinions, without doubt, have their origin in the papers by Scheurer-Kestner on this subject.

After having shown that the commercial platinum apparatus used for concentrating sulphuric acid are corroded in every part, the more so as the concentration is pushed further (Scheurer-Kestner, *Bull. Soc. Chim.*, 1875, [2], xxiv., p. 501; 1878, xxx., p. 28; *Comptes Rendus*, lxxvii., p. 1082), Scheurer-Kestner returned to the subject, and announced that the solution of the platinum depended upon the presence of nitrous products; that a pure acid free from nitrogen does not attack platinum (*Comptes Rendus*, 1880, xci., p. 59).

Recently M. Conroy (*Journ. Soc. Chem. Ind.*, 1903, xxii., p. 465) carried out further experiments by heating strips of platinum-foil in sulphuric acid to about 250° to 280°, and he entirely refuted Scheurer-Kestner's results. At these temperatures, which are those of the acid in the retorts during distillation, the platinum is always attacked; different substances influence the progress of the attack; nitrous acid, and especially arsenious acid, have a retarding action; most other substances likely to be met with in commercial acids, such as SO_4Pb , SO_4Fe , NaCl , $\text{SO}_4(\text{NH}_4)_2$, &c., have either slightly accelerating actions, or none at all.

My experiments on the decomposition of sulphate of ammonium have led me to complete this research from the temperature of boiling pure sulphuric acid (338°), and that of the acid more or less charged with sulphate of potassium; I have given the results, not by the volume of acid employed, but in a uniform manner of one hour's attack on a surface of 1 square decimetre (50 sq. c.m. on each side of a sheet of platinum-foil); this valuation alone is logical, as it is evident that the attack must be proportional to the surface. I must here remark that from one experiment to another the results may vary considerably according to the rhythm of the boiling, which is impossible to regulate. The strips of platinum used were from 10 to 20 μ in thickness; they consisted of ordinary commercial platinum; during the course of the experiments they lost more than half their weight, and became very friable.

The attack of a strip of platinum in a porcelain or platinum crucible only takes place to a very slight extent; but if we put the same strips and acid into a flask and boil for half-an-hour, we observe that the acid becomes yellow, and gradually the colour becomes deeper until it takes that of red ochre. Under these conditions a square decimetre loses about 0.01 grm. per hour (0.008 to 0.012 grm.); if the attack were uniform the loss of thickness on each side would be about 0.05 μ ; in practice the metal is attacked unequally, and takes a dull appearance. The difference of the action, according to whether we operate in a wide open vessel like a crucible or a narrow one like a flask, is due entirely to the temperature, which only reaches 250° to 270° in the first case, because the acid evaporates so quickly, while it goes up to 338° in the second case, where the evaporation is very slight.

The influence of temperature is, in fact, considerable. At 350° to 355° (the boiling-point of 50 grms. SO_4H_2 + 10 grms. SO_4K_2) the loss of weight reaches as much as 0.04 to 0.05 grm., and at 365° to 370° (the boiling-point of 50 grms. SO_4H_2 + 20 grms. SO_4K_2) it goes as high as 0.12 to 0.13 grm. In this latter case, with a square decimetre of surface to be attacked, a few minutes is sufficient to cause the acid to take a yellow colour.

These results were obtained with pure commercial acid having no action on ferrous sulphate, which, when used as recommended by M. Berthelot in his lectures, will indicate the presence of 1/50,000th to 1/100,000th part of nitrous compounds, but such an acid reacts on sulphate of brucine, and will show the presence of a few millionths of these compounds.*

This amount appears to be insufficient to explain the solution of the platinum by catalytic action, and to remove all doubt in this respect I undertook a special research.

First of all, I freed the acid from its nitrous products by diluting it to a density of 1.4 and re-concentrating it several times; according to Fresenius this operation is sufficient, and, in fact, acid thus diluted and boiled, when treated with sulphate of brucine, gave no rose colour at all, or at most a tint so faint that the addition of a ten-millionth part of nitric acid made it incomparably more distinct. Now this acid, practically free from nitrous products, attacks the platinum strips in exactly the same manner as the original acid (0.008 grm.); when enriched by 1/50,000th, 1/25,000th, 1/10,000th, and 1/1000th part of nitric acid, it caused losses of platinum of 0.0075 grm., 0.0118 grm., 0.0083 grm., and 0.008 grm. respectively. If the nitrous products play a fermentary part, as thought by Scheurer-Kestner, we should expect to see the losses increase in the same proportion. In the same manner, by adding an excess of nitric acid to mixtures containing sulphate of potassium the speed of attack was not changed (0.133 grm. instead of 0.133 and 0.124 grm.).

On the other hand, sulphate of ammonium exercises the retarding action observed by Scheurer-Kestner in a most perfect manner. M. Conroy found this salt to be without any special action, but he operated at about 250°, and his acid was too slightly enriched with platinum on account of having been heated for an insufficient time for the retarding action to be observed. This effect at 338° is such that after obtaining a slight solution, the metal no longer changes weight† so long as there are still a few m.grms. of ammonia per 30 c.c. of acid, then the solution takes its normal course. This is all easily explained by the following experiment:—If to a sulphuric solution of platinum we add sulphate of ammonium and then boil, the metal (and not platinum-black) is precipitated almost integrally in the form of sponge; there are certain restrictions and special

* A sulphuric solution of sulphate of brucine at 0.20 grm. per cent is a very sensitive reagent for nitrous and nitric acids. A drop of water containing one millionth part of nitric acid, placed on a drop of this solution, takes a bright red colour round its periphery. Two c.c. mixed with 1 c.c. of Paris water gave a bright red colour which changed to bright yellow in twenty-four hours.

† Sometimes it even increases a little on account of a slight deposit of platinum from the solution.

phenomena due to the formation of solutions with different properties, which I hope to examine later on.

This precipitated metal which is deposited on the surface of the strips of platinum when they are present, then exercises its decomposing action on the sulphate of ammonium without the compact metal being sensibly affected.

If we operate in the presence of sulphate of potassium, we also observe the retarding effect, but not a total stoppage as with the acid alone. Thus with 20 grms. SO_4K_2 + 50 grms. SO_4H_2 , the losses of platinum per hour, in the presence of a little sulphate of ammonium, were successively 0.0230 grm., 0.0210 grm., 0.0175 grm., 0.0406 grm., and 0.0901 grm. instead of 0.13 grm. These experiments also do away with the necessity for the presence of nitrous compounds, sulphate of ammonium appearing to be the agent most apt to destroy them.*

If, instead of compact platinum in strips, we take spongy platinum, we can dissolve it entirely. One grm. of sponge from the calcination of the chloroplatinates of aniline, quinine, and ammonia at a red heat, lost respectively in boiling sulphuric acid in the course of the first hour 0.06 grm., 0.033 grm., and 0.033 grm. If we compare these results with those obtained with strips of platinum we must remember that the surface of attack in 1 grm. of the two latter calcined sponges hardly exceeds 3 to 4 square decimetres; from this we can calculate the effect of the two extremes—as a surface folded as much as possible or else as a collection of little balls. In the first we should have a strip of about 2 μ thickness, in the second case the grm. would be composed of 170 million spheres each of 8 μ diameter. These figures are evidently only rough approximations deduced from the action of the sulphuric acid, but they lead us to the idea that reciprocally a strip of platinum sufficiently thin might perhaps fill the catalytic rôle of sponges of which the calculated thickness is relatively considerable. As a matter of fact, strips of commercial platinum of about 0.16 μ in thickness, slightly crumpled, will inflame hydrogen, will at the ordinary temperature change a solution of formic aldehyde into carbonic anhydride, and will make a flameless lamp with organic vapours, ammonia, &c., almost as well and conveniently as spongy platinum itself. As for the reaction of the attack it is practically $4\text{SO}_4\text{H}_2 + \text{Pt} = (\text{SO}_4)_2\text{Pt} + 2\text{SO}_2 + 4\text{H}_2\text{O}$; a platinum salt is formed, easily recognised by the addition of chloride of potassium to sulphuric solutions diluted with one volume of water; the liquid is decolourised, and deposits only octahedra. Still, the amount of SO_2 formed, compared with the loss of platinum, leads us to suppose that a little more platinum (1/20th) is dissolved than agrees with the above formula.—*Bull. Soc. Chim.*, Series 3, vol. xxxv., No. 1.

WET AND CRUCIBLE-FIRE METHODS FOR THE ASSAY OF GOLD TELLURIDE ORES, WITH NOTES ON THE ERRORS OCCURRING IN THE OPERATIONS OF FIRE ASSAY AND PARTING.†

By W. F. HILLEBRAND and E. T. ALLEN.
(Continued from p. 101).

PART I. ASSAY OF CRIPPLE CREEK TELLURIDE ORES (continued).

Fire Assay.

Conduct of the Assay.

THE assays were all made in Battersea F crucibles, heated in a gas-fed melting furnace, as the muffle available was

far too small to admit crucibles of such size. A very satisfactory charge was found to be that given below, and it was adhered to throughout, except in a few cases where the litharge was reduced to four assay tons without any apparent difference in results.

Ore	1 assay ton (29.166 grms.)
Sodium bicarbonate	1 assay ton
Litharge	6 assay tons
Borax (fused) . .	10 grms.
Salt cover	

Neither iron nor nitre was used. In most cases the requisite amount of silver was added to give two and one-half to three times the weight of the gold. During the earlier stages of firing the temperature was purposely kept low, and it was not made high until escape of gas had nearly ceased. The buttons obtained were rather large for cupellation—about 25 grms. in weight—but it was felt that, by reducing a large amount of lead, the collection of all the gold would be more certain. The buttons were in all cases soft and malleable. Not every slag was assayed, since it was found that the gold losses here were very slight, in direct disagreement with Fulton's results on Cripple Creek tellurides (*Journ. Am. Chem. Soc.*, 1898, xx., 596; see also *prox.*, "Discussion of Results").

The larger number of tests were made by one of us (A.), but in order to have the check of another worker a number were made by his colleague (H.). The latter's results seem to be in general a little below those of A.—a fact probably explained by the employment of a somewhat higher temperature in cupellation. The powerful influence of slight changes in temperature on the cupellation results will be emphasised in the second part of this paper.

Charges Used in Assaying Slags and Cupels.

The charge used for the slag assay was:—Litharge, 1 A.T.; argol, 2 grms.; salt. For cupels it was:—Litharge, 2 A.T.; soda, 1 A.T.; borax glass, 1.5 A.T.; argol, 2 grms.; salt.

Assays for Gold and Silver together.

The first assays were made in order to ascertain, not only the gold, but also the silver content of the ores, though no importance was attached to the determination of the latter. Incidentally these tests showed the losses of gold in slags and cupels.

Discussion of Results.—The cupellation loss, even without that due to volatilisation, is here seen to be markedly greater than in the slag. This observation is in agreement with the general tenor of statements found in the literature, but directly contradicts Fulton's statement, already referred to, as to telluride ores from Cripple Creek (*Journ. Am. Chem. Soc.*, 1898, vol. xx., p. 596). May not his high losses in the slag have resulted from his employment of iron nails, with resultant formation of auriferous sulphide in the slag?

In order to have a check upon the actual loss, including that due to volatilisation, proof metal of the composition of that obtained from the ore was cupelled with 25 grms. of lead. The results are given in Table IV.

When cupellation takes place at a low temperature, with formation of considerable feather litharge, as in the above cases, the loss by volatilisation is seen to be practically negligible, or if not absolutely inconsiderable to be compensated perhaps by retention of lead, but that the case is different when the temperature is higher is plainly shown elsewhere in this paper (Tables VIII. and IX.).

Assays for Gold alone.

In all these cases the requisite amount of silver was added at the start to give a bead suitable for parting. (See Table V.).

In order to check the actual loss, including that by volatilisation, cupellations were made with alloys corre-

* It is not absolutely certain that the last few millionths are destroyed when we distil the acid with a few thousandths of sulphate of ammonium; at least this is so according to an experiment I made; both the distillate and the residue coloured sulphate of brucine. It remains to be seen, however, whether the very feeble colouration observed is really due to nitric acid.

† United States Geological Survey. *Bulletin* No. 253. (Series E, Chemistry and Physics, 44).

sponding to the above and about 25 grms. in weight. (See Table VI.).

When the above percentage recoveries are compared with corresponding ones for the alloy far richer in gold (Table IV.), it is seen, as might be expected, not only that

TABLE III.—*Crucible Assays of Cripple Creek Telluride Ores for Gold and Silver together.*

(Values are the weights obtained in m.grms., and denote ounces per ton of 2000 pounds).

Main assay, Au + Ag.	Slags.		Cupels.	
	Au + Ag.	Au.	Au + Ag.	Au.
a	16'54	—	—	—
	16'37	0'07	—	—
	16'97	0'04	—	—
	16'50	—	—	—
	16'58	—	—	—
	16'54	—	—	—
Average ..	16'58	0'055	—	—
From slag ..	0'055	—	—	—
From cupel ..	0'085	—	—	—
Total	16'72	—	—	—
Less average gold from Table VII.	14'53	—	—	—
Silver	2'19	—	—	—
b	20'54	—	—	—
	20'63	0'08	—	—
	20'58	0'08	—	—
	20'88	—	—	—
	20'21	—	—	—
Average ..	20'57	0'08	0'015	—
From slag ..	0'08	—	—	—
From cupel ..	0'10	—	—	—
Total	20'75	—	—	—
Less average gold	17'75	—	—	—
Silver	3'00	—	—	—
a ₁	17'39	0'43	—	—
	17'40	0'05	—	—
	17'43	0'07	—	—
	17'25	0'03	—	—
Average ..	17'37	0'145	0'027*	—
From slag ..	0'145	—	—	—
From cupel ..	0'16	—	—	—
Total	17'675	—	—	—
Less average gold	15'60	—	—	—
Silver	2'075	—	—	—
b ₁	22'33	0'06	—	—
	22'34	0'05	—	—
	22'42	0'06	—	—
	22'38	0'04	—	—
Average ..	22'37	0'05	0'027*	—
From slag ..	0'05	—	—	—
From cupel ..	0'18	—	—	—
Total	22'50	—	—	—
Less average gold	19'63	—	—	—
Silver	2'87	—	—	—

* Averages obtained by combining all the beads (8) from a₁ and b₁.

TABLE IV.—*Cupellation Losses on Proof Alloy.*

	Taken.		Found.		Loss.		Recovered from cupels.	
	M.grms.	M.grms.	M.grms.	Per cent.	M.grm.	Per cent.	M.grm.	Per cent.
Ag	2'09	—	—	—	—	—	0'06	2'87
Au	15'59	—	—	—	—	—	0'077	0'49
Au + Ag	17'68	17'53	0'15	0'85	0'137	—	—	—
Ag	2'26	—	—	—	—	—	0'08	3'54
Au	15'74	—	—	—	—	—	0'077	0'49
Au + Ag	18'00	17'84	0'16	0'89	0'157	—	—	—
Ag	2'28	—	—	—	—	—	0'07	3'07
Au	19'75	—	—	—	—	—	0'08	0'40
Au + Ag	22'03	21'51	0'52	2'36	0'15	—	—	—
Ag	2'58	—	—	—	—	—	0'10	3'88
Au	19'64	—	—	—	—	—	0'07	0'36
Au + Ag	22'22	22'07	0'15	0'68	0'17	—	—	—

TABLE V.—*Crucible Assays of Cripple Creek Telluride Ores for Gold alone.*

(Values are the weights obtained in m.grms., and denote ounces per ton of 2000 pounds).

Main assay, Au.	Slags.		Cupels.	
	Au + Ag.	Au.	Au + Ag.	Au.
a	14'50	0'25	—	—
	14'42	0'36	—	—
	14'45	0'16	—	—
	14'47	0'18	—	—
Average	14'46	0'24	0'02	—
From slag and cupel	0'05	—	—	—
Total	14'51 (Allen).	—	—	—
a	14'63	—	—	—
	14'63	—	—	—
	14'53	—	—	—
	14'21	—	—	—
From slag and cupel	14'50	—	—	—
	0'05	—	—	—
Total	14'55 (Hillebrand).	—	—	—
a ₁	15'50	0'08	—	—
	15'52	0'09	—	—
	15'55	—	—	—
	15'61	—	—	—
	15'57	—	—	—
	15'53	—	—	—
Average	15'55	0'09	0'04	—
From slag and cupel	0'07	—	—	—
Total	15'62 (Allen).	—	—	—
a ₁	15'50	*	0'02	—
	15'48	—	—	—
Average	15'49	—	0'02	—
From slag and cupel	0'08	—	—	—
Total	15'57 (Hillebrand).	—	—	—
b	17'76	0'32	—	—
	17'83	0'28	—	—
Average	17'79	0'30	0'02	—
From slag and cupel	0'05	—	—	—
Total	17'84 (Allen).	—	—	—

TABLE V. (continued).

Main assay, Au.	Slags.		Cupels.	
	Au + Ag.	Au.	Au + Ag.	Au.
b	17.69	* 0.02	—	0.03
	17.73	* 0.02	—	0.03
	17.47	* 0.03	—	0.03
	17.14†	* 0.03	—	0.03
Average	17.63	—	0.025	—
From slag and cupel	0.055	—	—	0.03
Total	17.685 (Hillebrand).			
b ₁	19.39	0.14	—	1.48 0.05
	19.53	0.14	—	1.34 0.06
	19.51	—	—	1.28 0.03
	19.57	—	—	1.29 0.04
	19.55	—	—	—
	19.62	—	—	—
	19.56	—	—	—
Average	19.54	0.14	0.04	1.35 0.045
From slag and cupel	0.085	—	—	—
Total	19.625 (Allen).			
b ₁	19.79	*	—	—
	19.48	*	—	—
Average	19.63	—	0.02	—
From slag and cupel	0.07	—	—	0.05
Total	19.70* (Hillebrand).			

* Not weighed.

† Excluded from average, as undoubtedly low.

‡ Proof metal (19.85 m grms. gold and 49 m grms. silver) was crucibled, cupelled, and parted at the same time as these last two assays. The final gold was 19.84 + 0.07, or 19.91 in all, showing that in this case there must have been a marked retention of silver after parting. If a like correction has to be applied to the regular assays, the average drops to 19.64, almost exactly that of Allen.

TABLE VI.—Cupellation Losses on Proof Alloy.

	Taken.		Loss.		Recovered from cupels.	
	M.grms.	M.grms.	M.grms.	Per cent.	M.grms.	Per cent.
Ag ..	48.03	46.90	1.13	2.35	0.82	1.71
Au ..	15.79	15.70	0.09	0.57	0.02	0.12
Ag ..	55.37	54.77	0.60	1.08	—	—
Au ..	15.82	15.75	0.07	0.44	—	—
Ag ..	63.65	62.27	1.38	2.17	1.09	1.71
Au ..	19.72	19.63	0.09	0.46	0.02	0.10
Ag ..	63.81	62.46	1.35	2.11	1.04	1.63
Au ..	19.74	19.64	0.10	0.51	0.03	0.15

TABLE VII.—Comparison of Results by the Two Methods.

	Combination assay.	Fire assay.	
	Hillebrand.	Hillebrand.	Allen.
a	14.76*	14.55 (Average, 14.53†)	14.51
b	17.71	17.69 (Average, 17.75†)	17.84
a ₁	15.50	15.57 (Average, 15.61†)	15.62
b ₁	19.47	19.64 or 19.70 (Averages, 19.63† or 19.64†)	19.62 or 19.62‡

* Probably a little high from retained silver.

† Averaged from the results of both Hillebrand and Allen by giving proper credit for the number of tests made by each.

‡ See footnote to Table V. for explanation of the alternative value.

there is a selective absorption of the metals, but also that the gold loss by cupellation is absolutely, and, relatively to the silver, greater in the richer gold alloy; but it is singular that whereas in the latter case practically all the lost gold (and silver) seemed to be recovered from the cupel, in the case of the rich silver alloy by far the greater part of the lost gold has been volatilised instead of absorbed. That a portion, and relatively a large portion, is always thus volatilised under similar conditions the results given in Table IX. clearly show, but there the volatilisation loss, no matter at what temperature in the muffle, though very variable, is with one exception considerably below that by absorption. The explanation of this disagreement we are, unfortunately, unable to offer.

Comparison of Results.

Comparing the average results by combination wet and fire test and by fire assay alone, we have the results shown in Table VII.

From the above, it would seem to be clear, as claimed by Furman, that for telluride ores of the composition of those of Cripple Creek, the crucible fire assay gives results perfectly satisfactory as compared with wet extraction. In three of the four ores assayed by us the advantage would seem to lie very slightly with the fire assay, but the determinations are too few in number and not sufficiently uniformly in one direction to permit us to regard this as demonstrated.

Because possibly some one may raise the objection that the fire assay failed to extract from the residues insoluble in the liquid reagents the whole of their gold contents, and that therefore the results do not prove the accuracy of the fire assay in comparison with the other, it is to be regretted that recourse had to be taken to the former to complete the wet assays, but there seemed no help for it. No reasonable person will entertain any doubt on the subject.

(To be continued).

CONDENSATION COMPOUNDS OF CAMPHOR- OXALIC ACID AND AMINES.*

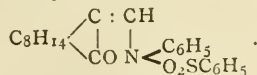
SEVENTH COMMUNICATION ON CAMPHOROXALIC DERIVATIVES.

By J. BISHOP TINGLE, Ph.D., F.C.S.,
and
WILLIAM EDWIN HOFFMAN, Jun., Ph.D.

(Continued from p. 102).

ACTION OF ACYLATING AGENTS ON CAMPHOFORMENE DERIVATIVES.

THE condensation compounds from primary amines described in the preceding pages, and those previously prepared by Bishop Tingle, are represented as containing an imino-group. This view of their constitution was based on the nature of the compounds formed from hydroxylamine and phenylhydrazine. It is very desirable to obtain some direct evidence on this point, and, consequently, the study of acylating agents on camphoformene derivatives was commenced. Bishop Tingle had previously shown that, with phenylsulphonic chloride, by the Schotten-Baumann reaction, phenylcamphoformeneamine forms a compound which crystallises from benzene in colourless needles and melts at 133°, but its composition was not determined. This work was repeated and a similar compound was obtained; it melted at 133°, and, on standing in the air soon began to decompose. It was found to be the *phenylcamphoformeneaminephenylsulphone*.—



* From the *American Chemical Journal*, xxxiv., No. 3.

Amines.	$C_8H_{14} \begin{smallmatrix} < C : COONH.R \\ \\ CO NHR \end{smallmatrix}$	$C_8H_{14} \begin{smallmatrix} < C : COOH \\ \\ CO NHR \end{smallmatrix}$	$C_8H_{14} \begin{smallmatrix} < C : CCH \\ \\ CO NHR \end{smallmatrix}$
I. $C_{10}H_{17}.NH_2$ β	169°	*M. p. 172° 5'	173°
II. $C_6H_4.CH_3.NH_2$ [1 : 4]	152°	168°	178°
III. $C_6H_5.CH_2.NH_2$	147° 5'	140°	96° 5'
IV. $C_{10}H_{17}.NH_2$ α	165°	*170°	—
V. $CH_3C_6H_4NH_2$ [1 : 3]	126°	154°	—
VI. $NH(C_2H_5)_2$	+139° 5'	—	153°
VII. $NH(CH_3)_2$	+137° 5'	—	63°
VIII. NH_2CH_3	172°	—	131°
IX. $C_6H_5C(NH_2):NH$	—	—	— (a)
X. $NH_2C_6H_4.C_6H_4NH_2$	—	—	— (b)
XI. $CH_3C_6H_3NH_2.NO_2$	—	—	192°
XII. $NH_2CONHNH_2$	200° and 209—210°	—	—
XIII. $C_6H_5NH_2$	*158°	*174°	*166°
XIV. NH_2OH	—	+146° 5'	—
XV. NH_3	—	*178°	—
XVI. $C_6H_4(NH_2)_2$ [1 : 2]	—	—	— (c)
XVII. $NH_2NHC_6H_5$	—	—	— (d)
XVIII. $CH_3CONHNHC_6H_5$	—	—	—
XIX. $OC(NH_2)_2$	—	—	—
XX. $NH_2C_6H_4NO_2$ [1 : 4]	—	—	—
XXI. $CH_3COC_6H_4NH_2$ [1 : 4]	—	—	—
XXII. $C_6H_5NHCH_3$	—	—	—
XXIII. $C_6H_5NHC_2H_5$	—	—	—
XXIV. $C_6H_5NHCH_2C_6H_5$	—	—	—
XXV. $C_2H_4(NH_2)_2$	—	—	—
XXVI. $C_6H_5NHNHCH_2C_6H_5$	—	—	—
XXVII. $(NH_2)_2C:NH$	—	—	—
XXVIII. $CH < \begin{smallmatrix} CH.CH \\ CH.CH \end{smallmatrix} > N$	—	—	—
XXIX. $C_6H_5N(CH_3)_2$	—	—	—
XXX. $CH_3C_6H_4NH_2$ [1 : 2]	—	—	—
XXXI. $NH_2NHC_6H_4Br$ [1 : 4]	—	—	—
XXXII. NH_2NH_2	—	—	—

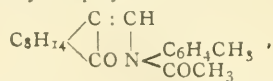
(a) $C_{19}H_{24}N_2O_4$. 184°.

(b) $C_8H_{14} \begin{smallmatrix} < C : COONH_3 \\ | \\ CO NH \\ | \\ C_6H_4C_6H_4 \end{smallmatrix}$. 190°.

(c) $+C_{18}H_{20}N_2O_2$. 246°.

(d) $+C_8H_{14} \begin{smallmatrix} < C : COOC_2H_5 \\ | \\ CO NHNHC_6H_5 \end{smallmatrix}$. 212°.

Acetyl chloride, when allowed to react with *p*-tolylcamphorformeneamine, replaces the iminic hydrogen and forms acetyl *p*-tolylcamphorformeneamine,—



which is a colourless crystalline compound melting at 161°. The reaction of these two chlorides with the above typical camphorformeneamines, resulting in the elimination of hydrochloric acid and the formation of the sulphone and acetyl derivatives, seems to be rather conclusive evidence in favour of the structure which has been suggested for the camphorformeneamines, and as we know that these bodies are formed from the corresponding carboxylic acids by the elimination of carbonic anhydride, the formulæ assigned to these acids also seem to be confirmed.

Chloracetyl chloride, when allowed to react with β -naphthylcamphorformeneamine, yields a colourless crystalline compound melting at 63°; unfortunately, on account of its instability, it could not be analysed.

The accompanying table shows the various condensation compounds of camphoroxalic acid and amines which have hitherto been prepared. They are arranged in type classes, and their melting-points are given. The compounds marked * have been previously described by J. Bishop Tingle and Alfred Tingle (*Journ. Am. Chem. Soc.*, 1901, xxiii., 364). Those marked + contain the elements of 1 molecule of water more than is shown in the type formula. Their constitution has been already discussed. In cases where no definite compound could be isolated, the space in the table is occupied by a dash.

EXPERIMENTAL.

Camphoroxalic acid was prepared according to the method worked out by J. Bishop Tingle (*Ibid.*, 1901, xxiii., 364) as follows:—

Camphor (31.5 grms.) and ethyl oxalate (22 grms.) were dissolved in 400 c.c. of anhydrous petroleum ether of 85—100° boiling-point and 3.5 grms. of sodium wire were added. The mixture was boiled on a water-bath with a reflux condenser until the violent action had ceased and the sodium had almost entirely dissolved; it was then allowed to remain over-night at the ordinary temperature, protected from moisture. The solution, after standing, was well shaken with about an equal volume of ice-water and the petroleum ether extract separated from the water and dried over calcium chloride. The dried liquid was distilled, at first from the water-bath; when the temperature of the boiling liquid rises to almost 90° the pressure is somewhat reduced and the distillation continued, care being taken not to allow the temperature of the liquid in the flask to rise above 130°; frequently it is unnecessary to heat above 120—125°.

The aqueous solution was then well cooled and acidified with dilute sulphuric acid, then extracted three or four times with ether, until a portion of the fresh ether extract showed only a pale reddish violet colour with alcohol and ferric chloride. The ether was dried over calcium chloride, and, after filtering, was distilled off, and the residue added to that from the petroleum ether extract. This residue was extracted several times by boiling with a 10 per cent solution of potassium hydroxide until the filtrate, after acidification, no longer gave a marked colour with alcohol and ferric chloride. The alkaline solution from the filtered

extracts was then acidified with dilute sulphuric acid, and, after standing several hours, the crystalline precipitate was filtered off. This crystalline mass was purified by re-crystallisation from petroleum ether by means of a Soxhlet apparatus. The mother-liquors from the re-crystallisations and the residue in the Soxhlet apparatus were treated with sodium carbonate, the solution filtered, acidified, and the resulting precipitate re-crystallised.

CAMPHOROXALIC ACID DERIVATIVES.

Metallic Salts of Camphoroxalic Acid.

Copper Camphoroxalate.—The acid (1 molecule) and copper nitrate (0.5 molecule) were separately dissolved in 50 per cent alcohol, the solutions mixed and allowed to evaporate at the ordinary temperature. Although the pure and dry copper salt does not melt below 275°, it was found that, if the solution was heated on a water-bath to remove the excess of alcohol, the green salt formed with part of the solvent an oily layer which was extremely difficult to purify. When it is allowed to crystallise at the ordinary temperature, it is deposited as a fine, green, crystalline powder, which melts and decomposes at 275°. With ferric chloride in alcoholic solution this salt gives no colouration. If an alcoholic solution of the salt is heated for some time at 100°, it undergoes decomposition and deposits cuprous oxide.

Analysis.—2.1686 grms. salt gave 0.0474 grm. CuO.

Calculated for $\text{C}_8\text{H}_{14}\left\langle \begin{array}{c} \text{C} : \text{COCOO} \\ \\ \text{CO} \end{array} \right\rangle \text{Cu}$	22.28
Found	22.46

The proportion of the reacting substances was varied, in the hope that another salt of different composition might be formed, but in all cases the resulting compound was identical with the one described above.

2. Silver Camphoroxalate.—Silver nitrate and camphoroxalic acid were allowed to react in a solution of 50 per cent alcohol, and, on allowing the solvent to evaporate spontaneously, a colourless crystalline mass was obtained, which was purified by repeated re-crystallisation from alcohol. The resulting compound was found to melt and decompose at 137°.

Analysis.—0.2975 grm. salt gave 0.0965 grm. Ag.

Calculated for $\text{C}_8\text{H}_{14}\left\langle \begin{array}{c} \text{C} : \text{COHCOOAg} \\ \\ \text{CO} \end{array} \right\rangle$	32.63
Found	32.47

As in the preparation of the copper salt, different proportions of silver nitrate and camphoroxalic acid were allowed to react, but in this case also only one compound could be isolated.

3. Barium Camphoroxalate.—Barium nitrate (1 molecule) and camphoroxalic acid (2 molecules) in a solution of 50 per cent alcohol were allowed to evaporate. These deposited a colourless crystalline compound, which was re-crystallised from alcohol. With ferric chloride and alcohol a reddish violet colour, characteristic of the presence of the enol grouping, was produced.

Analysis.—0.1728 grm. salt gave 0.0682 grm. BaSO₄.

Calculated for $\left(\text{C}_8\text{H}_{14}\left\langle \begin{array}{c} \text{C} : \text{COHCOO} \\ \\ \text{CO} \end{array} \right\rangle \right)_2 \text{Ba}$	23.56
Found	23.21

The proportions of the reacting substances were varied, as in the preceding cases, but no other salt could be obtained.

4. Calcium Camphoroxalate.—Calcium nitrate (1 molecule) and camphoroxalic acid (2 molecules) were mixed in solution of 50 per cent alcohol, under the same conditions

as in the case of the barium salt; on evaporation and re-crystallisation from alcohol, colourless crystals were deposited.

Analysis.—0.2067 grm. salt gave 0.0537 grm. CaSO₄.

Calculated for $\left(\text{C}_8\text{H}_{14}\left\langle \begin{array}{c} \text{C} : \text{COHCOO} \\ \\ \text{CO} \end{array} \right\rangle \right)_2 \text{Ca}$	8.22
Found	8.4

In the case of the calcium salt also, only one compound could be obtained.

5. Ferric Camphoroxalate.—Ferric chloride (1 molecule) and camphoroxalic acid (2 molecules) were mixed in solution of 50 per cent alcohol. A deep reddish violet colouration was produced, but from no solvent could a crystalline compound be obtained, and the viscous substance deposited by the evaporation of the original liquid to dryness gave percentages of iron which showed that it had no definite composition; hence the following method was employed:—The alcoholic solution of the reaction-product formed by the camphoroxalic acid and ferric chloride was diluted with water, in order to precipitate any unchanged camphoroxalic acid, and, at the same time, to dissolve the dark red substance in solution in the alcohol. After filtering, ether was added to the liquid, but, on account of the presence of free hydrochloric acid which had been formed by the reaction of the camphoroxalic acid and ferric chloride, the ether dissolved and formed a homogeneous solution with the original liquid. When this mixed ethereal aqueous liquid was saturated with sodium chloride, the ether took up the red compound and separated from the aqueous layer; this latter was removed, and the ethereal solution dried over calcium chloride. The ether was then evaporated from the water-bath. A glassy almost black mass remained. It is soluble to a slight extent in boiling sodium carbonate solution. The compound should, probably, be regarded as being camphoroxalic acid, in which the hydrogen atom of the enol group :COH has been replaced by iron, while the carboxyl group remained intact on account of the presence of hydrochloric acid in the liquid during the reaction.

Analysis.—0.2095 grm. substance gave 0.0235 grm. Fe₂O₃.

Calculated for $\left(\text{C}_8\text{H}_{14}\left\langle \begin{array}{c} \text{C} : \text{COCOHH} \\ \\ \text{CO} \end{array} \right\rangle \right)_3 \text{Fe}$	7.72
Found	7.8
(To be continued).	

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 23rd, 1906.

Prof. J. PERRY, F.R.S., President, in the Chair.

A PAPER by Mr. J. WALKER entitled "A Note on Talbot's Lines," was read by the SECRETARY.

The diffraction-pattern of a line of monochromatic light seen in focus, due to a rectangular aperture with its sides parallel to the line, is characterised by dark bands arranged at equal intervals on either side of the geometrical image of the line. The effect of covering half of the aperture with a retarding plate is to displace the bands of an odd order towards the covered side by an amount proportional to the retardation introduced, those of an even order remaining fixed. Suppose that the light is white and that its monochromatic constituents have been made by spectral analysis to occupy different angular positions in the field. Owing to the dispersion, the bands of an even order are

obliterated; but in the case of those of an odd order the dispersing power of the plate itself produces a dispersion of the bands, and consequently these bands will be seen, provided the plate have a suitable thickness and be so placed that the dispersion of the bands produced by it acts in opposition to the primitive dispersion of the light. The *modus operandi* may be clearly seen by supposing the phenomena analysed by a spectroscope having its slit in the plane of the diffraction-pattern in a direction perpendicular to the bands. A simple calculation gives the "best thickness" of the plate.

The Secretary showed photographs of Talbot's lines forwarded to him by Mr. W. B. Croft.

A paper on "Secondary Röntgen Radiation" was read by Dr. C. G. BARKLA.

In previous papers the author has shown that the secondary X-rays from certain gases and light solids subject to Röntgen radiation may be fully explained by considering the corpuscles or electrons constituting the atoms to be accelerated in the direction of electric displacement in each primary Röntgen pulse as it passes through such substances, and that the interaction between the electrons affects only to a slight extent the character of the secondary radiation. The methods of investigating the more complex secondary radiation from metals was suggested by the results of the experiments on lighter substances. The character of secondary radiation (measured by absorptivity) was found to depend on the atomic weight of the radiator. The radiation from compounds was in all cases such as would be given by a mixture of the radiations from the separate constituent elements. By heating an iron wire to white heat and studying the radiation proceeding from it when exposed to X-rays, it was seen that there was no direct connection between the intensity or character of the radiation and temperature, electric conductivity, or magnetic permeability. Experiments on absorption showed that the radiation from heavier atoms did not consist of an easily absorbed radiation superposed on a scattered radiation, such as proceeded from light atoms, but that the latter was not present to any appreciable extent.

No special absorption by a metal of the radiation proceeding from the same metal was observed. Thus there was no evidence of a definite periodic vibration. Changes in the character of the primary produced changes in the secondary. Variation in intensity of the primary beam was found not to affect the character of the radiation from calcium—the only substance experimented upon. When substances were exposed to polarised Röntgen radiation, the secondary radiations, which differed little in absorptivity from the primary producing them, showed approximately equal variations in intensity in different directions. The very different radiations exhibited no such variation; while the radiation from a substance of atomic weight between those of the two classes showed the variation to an intermediate extent. In this polarisation effect compounds behaved as mixtures of the constituent elements. Experiments on the absorption of rays proceeding from thick plates of a large number of elements showed that beyond the region of atomic weights in which the character of the secondary radiation is almost independent of the nature of the radiation, the absorptivity is a periodic function of the atomic weight of the radiator, and that as far as these experiments have gone different periods are represented by curves of similar form. The theory which has been found to explain all the phenomena of secondary radiation from light atoms may be extended to explain these results, if we conceive the independence of motion of the electrons to disappear with an increase in the number of electrons in the atom. Inter-electronic forces called into play make the pulses emitted by each electron thicker than if the electron were accelerated only during the period of passage of the primary pulse over it. Hence the radiation becomes less penetrating. Only agencies altering the construction of the atom would be expected to change the character of the radiation produced

by a given primary; hence, temperature, electrical resistance, magnetic permeability, may all vary without producing appreciable effect. The theory also explains the disappearance of the more purely scattered radiation, the absence of selective absorption, the connection and difference between the primary and secondary rays, and the absence of influence of variation in intensity of primary radiation on absorptivity of the secondary. When applied to the atom as conceived by Prof. J. J. Thomson, the periodicity shown by the curve connecting absorption and atomic weight is explained.

A paper by Messrs. C. W. S. CRAWLEY and F. B. O. HAWES entitled "*Records of the difference of Potential between Railway Lines when a Train passes and at other times, and a suggested Method for the observation of Earth Currents and Magnetic Variations,*" was read by Mr. CRAWLEY.

The experiments described in the paper were made on the London and South Western main line, between Walton and Weybridge stations. To each rail of the up line a wire was permanently attached, and the other ends of the wires were connected to the terminals of a reflecting galvanometer. The deflections of the galvanometer were recorded on a moving sheet of paper, and curves obtained showing the variation in the current through the galvanometer. The curves showed a concordance in the results from successive trains. The normal current through the galvanometer began to be disturbed about one minute before the passage of a train, and the disturbance lasted about two minutes. The curves, although very complex, showed some regularity. In addition to the disturbances caused by passing trains, very distinct smaller disturbances were noticeable at the times when a receding train was passing over the points at Walton and Esher stations. Effects were also shown corresponding with the passage of a train over the Hampton Court Junction points. The observations on different occasions varied in many respects, the state of the weather probably being an important factor. The E.M.F. between the rails was on one occasion as much as 28 millivolts, and differences of 8 and 15 millivolts were frequent. It appears probable to the authors that the effects are due to earth currents, and they suggest that by making the galvanometer very sensitive its deflections might furnish a means of studying their variation.

Dr. C. CHREE expressed his interest in the paper, and remarked that it was often more desirable to avoid earth currents than to record them. He questioned whether the effects described by the authors were due to earth currents, and asked if the authors had satisfied themselves that the variations in the galvanometer deflections were not due to magnetic storms.

Dr. J. A. HARKER described some experiments similar to those made by the authors. In his case, wires from a galvanometer were connected to two large plates about 200 yards apart and about 5 feet underground. He found that the effects varied with the weather.

INSTITUTE OF CHEMISTRY.

Annual General Meeting, March 1st, 1906.

Mr. DAVID HOWARD, President, in the Chair.

THE Accounts for 1905 having been submitted by the Hon. Treasurer, Mr. A. GORDON SALAMON, and duly received, Dr. JOHN A. VOELCKER moved the adoption of the Annual Report. He congratulated the Council on their work during the past year, and he specially alluded to the steps they had taken to protect the interests of professional chemists. Mr. ARTHUR E. EKINS seconded, and the Report was formally received and adopted.

Scrutineers having been appointed to count the votes sent in for the election of the Officers and Members of Council, and ballot having been taken for the election of

Censors, the Meeting proceeded to select the Honorary Auditors, and Messrs. Robert E. Alison, W. T. Burgess, and P. A. E. Richards were appointed.

The PRESIDENT then delivered his Address. After referring to the progress made by the Institute during his term of office as President, he dealt more particularly with the history of the third and last year.

While the roll of Fellows and Associates has steadily increased, he noted with regret the death of some of the original Fellows, and he mentioned especially John Lloyd Bullock, largely to whose incentive was due the foundation of the Royal College of Chemistry and the invitation to Hofmann to come to London. How much that meant to not a few, including several Past-Presidents of the Institute, it would take long to tell.

The Institute was examining over 100 candidates yearly, and arrangements would be made from time to time for examinations in the Colonies.

Mr. Howard alluded to the improvement in the financial position of the Institute and to the steady growth of the library. He paid a high tribute to the services of Prof. Adrian J. Brown, who has held the appointment of Examiner to the Institute in Biological Chemistry since 1901, and stated that, as his term of office had expired, the Council had selected Dr. Arthur Harden, of the Lister Institute, as his successor.

He also referred to the new examinations in Technical Chemistry, the first of which will be held in October next. In this connection he expressed the hope that the Institute would in future have for its presidents industrial chemists as well as those eminent for educational and strictly professional work. The chief function of the Institute was to register competent consulting analytical and technical chemists, and the Institute might safely claim to represent the profession. The Council regarded it as their duty to advance the interests of the profession, and, as far as they were able, to maintain it on a sound and satisfactory basis. They had lately been obliged to make representations to authorities whose actions appeared to be detrimental to the profession.

With reference to the gratuitous performance of analyses at Agricultural Colleges, he mentioned that the Board of Agriculture had endeavoured to show that the performance of cheap milk tests had been arranged for educational purposes. At the same time, the Board had stated that these tests were not seriously to be compared with the analyses made by Public Analysts and district analysts. The Council had to complain of more than the milk tests—the Colleges were undertaking all kinds of analyses at nominal fees; of soils, for instance, at half-a-crown. This was undoubtedly injurious to the profession, but the Board in its journal stated that "the demand on the part of landowners for expert advice from the lecturers had been considerably in excess of what might reasonably have been anticipated." In this matter, the Council had not received a satisfactory response.

He referred to the great advances in chemistry that had been due to the work of private practitioners, giving his opinion that any action which tends to interfere with the individual practitioners would be fatal to progress.

It was with reluctance that the Council had to take up an attitude which might seem in any way antagonistic to the National Physical Laboratory, but they had been obliged to direct the attention of the Executive Committee to the fact that their test pamphlet indicated that they might undertake work which they were forbidden to undertake under the Treasury Report on which the Laboratory was founded. The Executive Committee has recently given their assurance of their desire to avoid any cause for complaint. He was sure that the Council would be glad to see the Laboratory placed on such a sound footing financially that its authorities would have no temptation to extend the work of the Laboratory beyond its proper sphere.

Mr. Howard thought the profession had reached a

somewhat critical stage in its history. With greater facilities for training, and, consequently, a larger supply of chemists, it was evident that only the most efficient could hope to be successful. He believed the demand for chemists was increasing, but authorities and manufacturers were learning that they must have efficiency.

After dealing briefly with the present position of the industrial chemist, and the official professional chemist, he referred to the professors and teachers of chemistry. He objected to the practice, which had grown of late, of blaming the Universities for the loss of certain industries. He maintained that, while chemists were improving so greatly in efficiency, it was absurd to blame the professors. Every decade does not bring a Hofmann, but there were many teachers at the present day under whom the bulk of Fellows and Associates were proud to say they had been trained.

The Institute afforded a great benefit to the public by aiding its discrimination in the selection of competent chemists of acknowledged ability and professional integrity; they could rely on each Fellow and Associate to further the reputation of the Institute by his character and conduct, the soundness of his work, and by the cultivation of professional feeling.

Mr. Howard then referred to the new President, Prof. Percy F. Frankland, who had long been associated with the Institute, and whose father, Sir Edward Frankland, was the founder and first President. He concluded by saying how much he had appreciated his position as President of the Institute, and he spoke in warm terms of the co-operation of the Councils with whom he had worked.

A vote of thanks for the Address was moved by Mr. THOS. TYRER, seconded by Prof. J. MILLAR THOMSON, supported by Mr. R. J. FRISWELL, and carried unanimously.

On the report of the Scrutineers the result of the balloting for the selection of Censors was submitted, and Mr. David Howard, Sir William Ramsay, K.C.B., F.R.S., Sir Thos. Stevenson, M.D., and Prof. J. Millar Thomson, F.R.S., were declared elected.

The Officers and Members of Council for the ensuing year were then declared elected as follows:—

President—Percy Faraday Frankland, LL.D., Ph.D., F.R.S.

Vice-Presidents—Edward John Bevan; Edward Divers, M.D., D.Sc., F.R.S.; David Howard; Edmund Albert Letts, D.Sc.; Edmund James Mills, D.Sc., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.

Hon. Treasurer—Alfred Gordon Salomon, A.R.S.M.

Members of Council—Adrian John Brown, M.Sc.; Lt.-Col. Charles Edward Cassal; Arthur Crozier Claudet, A.R.S.M.; John Norman Collie, Ph.D., F.R.S.; James Kear Colwell; Cecil Howard Cribb, B.Sc.; Henry John Horstman Fenton, M.A., F.R.S.; Martin Onslow Forster, D.Sc., F.R.S.; Richard John Friswell; William Gowland, A.R.S.M.; Arthur George Green; Henry George Greenish; Oscar Guttmann; James Hendrick, B.Sc.; Egbert Grant Hooper; Herbert Jackson; Arthur Robert Ling; Henry de Mosenthal; Henry Droop Richmond; Alfred Smetham; Arthur Smithells, B.Sc., F.R.S.; John Edward Stead, F.R.S.; David Alexander Sutherland; Francis Napier Sutton; Edward William Voelcker, A.R.S.M.; William Palmer Wynne, D.Sc., F.R.S.; Sydney Young, D.Sc., F.R.S.

On the motion of Lt.-Col. CHARLES E. CASSAL, seconded by Mr. P. GERALD SANFORD, a vote of thanks was accorded to the retiring Officers and Members of Council. The PRESIDENT having replied, the meeting terminated.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th inst., The Duke of Northumberland, K.G., President, in the Chair. Messrs. Frank Green, A. W. Oke, N. M. Ogle, H. F. Pooley, H. Taverner, and A. B. Thomas were elected Members.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 6, February 5, 1906.

Insoluble Potassium Compounds contained in the Trunk and Bark of Oak Trees.—M. Berthelot.—The author makes a series of experiments on the potassium salts found in the trunk and bark of oak trees. He finds that insoluble salts exist in very much smaller proportion than in the leaves, this being apparently due to the fact that the leaves are the terminus of the ascendant circulation of the liquids, and so receive an accumulation of insoluble matter.

Rotatory Power of the Hexahydrobenzylidene- and Cenanthyldene-camphors and their Corresponding Saturated Derivatives.—A. Haller and F. March.—The authors' experiments prove—(1) that the specific rotatory power of hexahydrobenzylidene and cenanthyldene camphors are considerably less than the rotatory power of the corresponding benzenic compounds; (2) that the rotation of the saturated acyl-derivatives is inferior to that of the corresponding non-saturated derivatives; (3) that the nature of the saturated lateral chains C_6H_{11} , C_6H_5 , whether they are cyclic or aliphatic, does not seem to sensibly modify the rotatory power in the two series respectively. The author therefore concludes that in benzylidene camphor and its analogues, in the same way as in benzyl camphors, it is the non-saturated character of the benzenic radical which exercises an action on the elevation of the rotatory power of the asymmetric molecule to which this radical is attached.

Condensation of Acetylenic Nitriles with Alcohols. General Method of Synthesis of β -Substituted β -Oxyalcoyl Acrylic Nitrites.—Ch. Moureu and I. Lazennec.—When an acetylenic nitrile, $R-C\equiv C-CN$, is put in contact with a solution of methylate or ethylate of sodium in the corresponding alcohol, a brisk reaction takes place. After heating for two or three hours and then cooling, an almost colourless oil is precipitated, which consists of a mixture in varying proportions of β -oxyalcoyl ethylenic nitrile and β -acetalic nitrile.

Attempted Reduction in the Diphenylmethane Series.—H. Duval.—In a previous research the author described the method of preparation of azoxy- and azodiamino diphenylmethane, and he now describes his experiments on the influence of reduction and benzdination on these compounds.

Cyclohexylacetone.—P. Freundler.—For some time the author has made various unsuccessful attempts to prepare cyclohexylacetone, $C_6H_{11}.CH_2.CO.CH_3$. He now succeeds in obtaining this ketone, but with a poor yield. The various methods of preparation are described, the most successful being the condensation of hexahydrobenzyl magnesium iodide with acetic aldehyde, and oxidising the secondary alcohol thus obtained with the chromic mixture:—

$$C_6H_5.CH_2.MgI + CHO.CH_3 = C_6H_5.CH_2.CH \begin{smallmatrix} OMgI \\ CH_3 \end{smallmatrix}$$

$$C_6H_5.CH_2.CHOH.CH_3 + O = H_2O + C_6H_5.CH_2.CO.CH_3.$$

The secondary alcohol, of which the yield is about 40 per cent, is accompanied by superior products.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 1, 1906.

Arsenic Pentafluoride.—Otto Ruff and Hugo Graf.—Arsenic pentafluoride is best prepared in a platinum retort connected with an ascending platinum condenser, which leads to a platinum receiver, although glass vessels may be

substituted; they must, however, be carefully dried before use, and no rubber corks, &c., must be employed, because the presence of the least trace of organic matter leads to the formation of hydrofluoric acid. In the retort 0.2 mol. of cooled antimony pentafluoride, and 0.1 mol. of cooled arsenic trifluoride are placed, all moisture being carefully excluded. Then the mixture is cooled to -20° and $\frac{1}{4}$ mol. of cooled bromine is added. While the receiver is still cooled by means of liquid air, the retort is allowed gradually to acquire the temperature of the surroundings, and is finally heated to 55° for about half-an-hour on a water-bath. At the end of this time about the theoretical quantity of arsenic pentafluoride will be found in the receiver mixed with some bromine. To separate this latter, the mixture must be fractionated. For this purpose the receiver is removed, and connected with a similar receiver which has previously been very carefully dried, and the first receiver is taken out of the liquid air, while the second is cooled by the same agent. The distillation of the pentafluoride begins at once, and is finished when the vessel has acquired the temperature of the surroundings, nearly all the bromine remaining behind in the first vessel. To complete the separation, the distillation must be repeated. The reaction which occurs is represented by the equation: $2SbF_5 + AsF_3 \cdot Br_2 = 2SbF_4Br + AsF_5$. The authors have not investigated whether the antimony bromine fluoride is a simple compound or a mixture. Arsenic pentafluoride is a colourless gas, which condenses to a clear slightly yellowish liquid at -53° , and solidifies at -80° to a white mass. The gas dissolves in water and alkali solutions, much heat being evolved. Its great affinity for water is shown by the dense white clouds which are formed when it comes in contact with the air. It does not attack perfectly dry glass in the cold, but a violent reaction occurs if the least trace of moisture or of hydrofluoric acid is present. On heating, even dry glass reacts with the gas, silicon tetrafluoride being formed and a white volatile substance being separated, obviously consisting of arsenic pentoxide. Silicon does not react in the cold, but on heating, arsenic is separated and silicon tetrafluoride formed. Sulphur and arsenic pentafluoride react upon one another very slowly in the cold, the sulphur becoming first orange and then black, and finally a sticky mass is formed. This smells strongly of sulphur monochloride or bromide, but soon loses the smell in air, the black product simultaneously turning yellow and crystallising. Dry phosphorus is only slightly attacked, even on warming. Iodine reacts readily in the cold. Copper is not attacked in the cold, but blackens on warming. Zinc, iron, and bismuth darken on heating in the gas, obviously in consequence of the separation of arsenic and formation of fluorides. Lead and mercury react particularly energetically on heating. Tungsten is not affected. The pentafluoride is soluble in liquid arsenic trifluoride, heat being evolved to a slight extent. Generally a vigorous reaction occurs with organic substances. Dry paper and sugar are not altered by the gas, but the moist substances are rapidly charred. Paraffin and wax are somewhat more resistant, but are gradually blackened. The density corresponds approximately to the molecular weight represented by the formula AsF_5 .

Acceleration of certain Oxidation Reactions by Prussic Acid.—A. S. Loevenhart.—The author has come to the conclusion that the catalytic decomposition of hydrogen peroxide into water and molecular oxygen, and the indirect oxidations by means of hydrogen peroxide, are phenomena which are closely allied to one another. The grounds for this belief are:—(1) All substances so far investigated which catalyse hydrogen peroxide also give rise to indirect oxidations by means of hydrogen peroxide; (2) the two processes are equally influenced by temperature; (3) substances which retard one of these processes have the same effect on the other; e.g., prussic acid retards the catalysis of hydrogen peroxide by platinum black, and also the oxidations produced by means of hydrogen peroxide. This theory is confirmed by the investigation

of the oxidation of formic acid by means of hydrogen peroxide in presence of copper sulphate, which is accelerated by the presence of prussic acid. Apparently the more stable cupric compounds can be converted into cuprous compounds only by very strong reducing agents, while cupric cyanide is very rapidly reduced to the cuprous salt, and thus the acceleration is due to the formation of the cyanogen compound with copper. It is evident that prussic acid cannot be regarded as an anti-catalyser, and indeed it is, generally speaking, not possible to say definitely that any given substance is an anti-catalyser, for the same substance which accelerates the action of one catalyser may retard that of another.

Titrimetric Method for the Quantitative Determination of Pentoses.—Adolph Jolles.—The pentoses, or substances yielding them, are first converted into furfural by distillation with hydrochloric acid, and the furfural is driven over by a current of steam. An aliquot part of the distillate is neutralised and a measured quantity of bisulphite added, when the following reaction occurs:— $C_4H_3O.CHO + KHSO_3 = C_4H_3O.CH(OH).SO_3K$. Thus each molecule of furfural requires one molecule of bisulphite. After two hours the excess of bisulphite is titrated back with iodine solution; each c.c. of normal bisulphite corresponds to 75.05 m.grms. of pentose. The same method can be used for the determination of furfural.

Cyanuric Acid as Pseudo Acid.—A. Hantzsch.—Cyanuric acid dissolves to a clear solution in fairly concentrated caustic soda at the ordinary temperature, but from this solution, which does not appear supersaturated, and contains only secondary sodium salt, on heating tertiary salt is deposited, which is not dissolved by the mother-liquor at the ordinary temperature. The formula of the secondary salt is $[C(ONa):N]_2[CO.NH]$, and that of the tertiary $[C(ONa):N]_3$, and at the higher temperature the last group, $CO.NH$, of the secondary salt isomerises to $C(OH):N$, and is fixed as $C(ONa):N$. By the conductivity it may be shown that in an aqueous solution of trisodium salt at the ordinary temperature, one molecule of free soda is present. After evaporation of the solution at the ordinary temperature a mixture of disodium salt and free soda remains behind. This phenomenon may be regarded as an hydrolysis of the cyanurate, abnormally varying with the temperature. For the salts $C_3N_3O_3Me_3$ are at ordinary temperatures totally hydrolysed to $C_3N_3O_3Na_2H + NaOH$, but while with increasing temperature in normal cases the hydrolysis, on account of the greatly increasing dissociation of water, also increases; the opposite occurs here in consequence of the intramolecular transposition, $CO.NH + NaOH \rightleftharpoons C(ONa):N + H_2O$. A decrease of the hydrolysis of alkali salts as the temperature increases is thus a new criterion of an intramolecular transposition, or, in other words, a criterion whether the salts in question have been formed from a pseudo acid. This test is naturally applicable only in the case of those pseudo acids which are transposed into such feeble true acids that their alkali salts suffer appreciable hydrolysis.

Preparation of Trialkyl Stilbine, Arsine, and Phosphine by Grignard's Reaction.—Harold Hibbert.—Auger and Billy have found that by the action of magnesium ethyl bromide upon excess of phosphorus, arsenic, or antimony trichloride, no trialkyl compounds are formed, or only very small amounts. But if the trichlorides are allowed to react with three or more molecules of the magnesium alkyl compound in ethereal solution, a yield of up to 75 per cent of trialkyl derivative is obtained. This can then be distilled in a current of carbon dioxide. In the case of the phosphorus derivative the yield is very small unless a very large excess of magnesium ethyl bromide is used. The greater part of the triethyl phosphine does not distil over till a temperature of 160—200° is reached, which seems to show that it is not formed directly, as in the case of the arsenic or antimony compound, but that either brominated by-products or addition products result, and give up free triethyl phosphine

at the higher temperature. The yield of phosphine amounts to 70 per cent of the theory.

Action of Oxygen on Aliphatic Amines in presence of Copper.—Wilhelm Traube and Albert Schönewald.—In the presence of oxygen aqueous solutions of the primary amines, e.g., ethylamine, rapidly attack copper, and the base is oxidised, the alkyl group being converted into aldehyde, while the nitrogen splits off as ammonia. No nitrites could be detected either as final or by-products. The proportion of oxygen used for the oxidation of the copper and the formation of aldehyde was 1:1, half the oxygen being combined with the metal, while the other half attacks the amine. With methylamine formaldehyde is similarly obtained and free ammonia, no nitrous acid being formed.

Use of Hydrogen Peroxide for the Quantitative Separation of the Halogens.—P. Jannasch and Fr. Zimmermann.—The mixture of halogens is dissolved in water in a distillation flask, pure glacial acetic acid and hydrogen peroxide are added, and the mixture is then distilled in a current of steam. The iodine is driven over quantitatively in not more than twenty to twenty-five minutes, the liquid being completely decolorised in from three to five minutes. The iodine is received in a vessel containing water, uncrystallised hydrazine sulphate, and the strongest ammonia. After the distillation has been stopped the contents of this vessel are washed into a beaker, acidified with concentrated nitric acid free from chlorine, and precipitated with excess of silver nitrate solution in the cold, the resulting silver iodide being heated until it can be filtered readily. The bromine may be separated from the chlorine in the residue by the addition of large quantities of sulphuric acid, but the authors have not yet finished their investigation of this point.

Properties of Electrolytic Calcium.—L. Doerner.—The author found when experimenting with electrolytic calcium from the Bitterfeld Electrochemical Works that somewhat violent explosions occurred when he struck the metal sharply with a hammer on an anvil. The explosiveness is very much reduced, or is even removed altogether if implements are used which are perfectly free from rust and iron oxide. Working with a rusty anvil explosions were always obtained, while if hammer and anvil had been thoroughly rubbed with emery paper they seldom occurred. On gently warming the metal, before a red heat was reached, hydrogen was set free, and if the metal was then heated to a faint red heat all the gas was rapidly absorbed again. When the electrolytically prepared metal is ignited a glow passes through the mass, which fuses to a doughy melt, consisting of metallic calcium. A flame held over the melt during this process is coloured distinctly yellowish red by volatile calcium compounds. If this process is carried out in a crucible and the doughy mass is kneaded with an iron spatulum, gas flames appear and a calcium regulus is obtained, which after cooling is much more stable towards moist air than ordinary calcium. A piece of this calcium after lying in air for eight days showed no external change, while with ordinary calcium a large amount of hydrate was formed. The same behaviour was noticed towards water, and the unfused calcium is harder, more brittle, and of a yellower colour.

Preparation of Titanium Tetrachloride and Tin Tetrachloride.—Carl Renz.—By the action of carbon tetrachloride and heat upon certain oxides the following reactions occur:— $CCl_4 + MeO = MeCl_2 + COCl_2$, $CCl_4 + 2MeO = 2MeCl_2 + CO_2$. Thus when carbon tetrachloride is led over heated titanium dioxide, carbon dioxide or phosgene and titanium tetrachloride are formed. If chloroform is substituted for carbon tetrachloride this method is excellently suited for the preparation of titanium tetrachloride. The chief reaction proceeds as follows:— $TiO_2 + 2CHCl_3 = TiCl_4 + 2CO + 2HCl$, but according to the temperature various by-reactions also occur. Sometimes a colourless gas, presumably titanium hydride, TiH_4 , results, carbon dioxide and phosgene have also been

detected, and hexachlorbenzene. If stannic oxide is substituted for titanium dioxide, the corresponding tin tetrachloride is formed, but silicon tetrachloride cannot be prepared by the same method.

MEETINGS FOR THE WEEK.

- MONDAY, 12th.—Society of Arts, 8. (Cantor Lectures). "Fire, Fire Risks, and Fire Extinction," by Vivian B. Lewes.
- TUESDAY, 13th.—Royal Institution, 5. "Food and Nutrition," by Prof. William Stirling, M.D., &c.
- WEDNESDAY, 14th.—Society of Arts, 8. "Imperial Organisation from a Business Point of View," by Geoffrey Drage.
- THURSDAY, 15th.—Royal Institution, 5. "The Physiology of Plants," by Francis Darwin, M.A., &c.
- Society of Arts, 4.30. "The Languages of India and the Linguistic Survey," by Dr. George A. Grierson, C.I.E.
- Chemical, 8.30. "Interaction of well-dried Mixtures of Hydrocarbons and Oxygen," by W. A. Bone and G. W. Andrew. "Explosive Combustion of Hydrocarbons," by W. A. Bone and J. Drugman. "The occurrence of Marsh Gas amongst the Decomposition Products of certain Nitrogenous Bases as a Source of Error in the Determination of Nitrogen by the Absolute Method," by P. Haas. "Studies on Comparative Microscopy—Part IV. The Hydrocarbons and their Halogen Derivatives in Phenol Solution," by P. W. Robertson. "Displacement of Acid Radicles—I., Displacement of the Chloride and Nitrate Radicles," by A. F. Joseph.
- FRIDAY, 16th.—Royal Institution, 9. "How to Improve Telephony," by W. Duddell.
- SATURDAY, 17th.—Royal Institution, 3. "The Corpuscular Theory of Matter," by Prof. J. J. Thomson, F.R.S., &c.

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THE CHEMICAL NEWS.

VOL. XXIII., No. 2416.

REDUCTION OF SULPHURIC ACID AND OTHER SUBSTANCES.

By Dr. T. L. PHIPSON.

WHEN a piece of metallic sodium is allowed to fall into monohydrated sulphuric acid, sp. gr. 1.845, contained in a small porcelain capsule, the reaction is extremely violent, accompanied by a loud hissing sound, great heat, and copious projections of vapour. The chief product remaining in the porcelain capsule is a yellow sulphide of sodium.

A good many years have elapsed since I made this dangerous experiment, which requires the greatest precautions on account of the projections, and I never published it. Soon after I used metallic magnesium in my experiments of this kind (see my note on "Magnesium" in the *Proceedings of the Royal Society*). Thus I was the first to obtain, by the aid of a simple spirit-lamp, carbon from carbonic acid, boron from boric acid, silicium from silica, and zirconium from zirconia.

The carbon thus obtained from pure anhydrous carbonate of soda in a thin porcelain crucible, well closed, has not the aspect of graphite, nor anthracite, like that in the beautiful little quartz crystals from the mountain limestone at Maffles, in Belgium; but when the magnesia and soda that are present are washed out by a little weak hydrochloric acid, this carbon has the dull black appearance of pulverised wood-charcoal. A peculiar emission of light seen through the thin sides of the porcelain crucible announces when the reduction has taken place.

The silicium thus produced has a brownish colour, the boron also, but the zirconium has a peculiar velvet-black aspect.

M. Moissan stated a short time ago in the *Comptes Rendus* that this process of mine is the only one that yields absolutely pure zirconium.

THE NEUTRAL HYDROCHLORATE OF QUININE.

By H. CARETTE.

In a former paper (*Journ. de Pharm. et de Chim.*, [6], vol. xx., p. 347), on the neutral hydrochlorate of quinine, it was shown that this salt can be crystallised with alcohol of crystallisation. Shortly afterwards I learnt through the same Journal ([6], vol. xx., p. 550), that M. Biscaro had some years previously (*Boll. Farm.*, 1901, [4], vol. xl., p. 105), observed the presence of alcohol in certain crystals of the same salt. We both found losses identical in amount, on desiccating the salt crystallised in alcohol; viz., 14.33 to 14.34 per cent; but while I interpreted this result of the analyses by the loss of 1½ molecules of alcohol, or 14.80 per cent, M. Biscaro attributed the loss observed to the simultaneous presence in the salt of a molecule of alcohol and a molecule of water, that is to say 13.88 per cent. In view of this divergence in the interpretation of identical analytical results, I thought it advisable to repeat the examination of the crystallisation of the neutral hydrochlorate of quinine. I now give the results of my fresh experiments.

One result of my later experiments is that by the crystallisation in alcohol absolutely free from water, the neutral hydrochlorate of quinine furnishes crystals which had not previously been observed either by M. Biscaro or

myself. These crystals were in the form of white nodules containing only one molecule of alcohol of crystallisation. The neutral hydrochlorate of quinine, when crystallised in alcohol at 95 per cent, fixes simultaneously one molecule of alcohol and one molecule of water, as shown by M. Biscaro.

I have made a comparative examination of the products of the crystallisation of the neutral hydrochlorate of quinine in alcohol completely free from water, and in alcohol containing small quantities of water.

I first of all used alcohol completely dried by means of anhydrous baryta, preventing in all the operations any contact with moist air which might hydrate the alcohol.

The neutral hydrochlorate of quinine dried by means of a sufficiently prolonged exposure in an oven at 95°, was then dissolved in the hot absolute alcohol. On crystallising this alcoholic liquor by cooling, the salt is deposited as white opaque nodules, composed of fine needles.

In the oven at 95°, 0.65 grm. of this salt, well drained on filter paper, lost 0.0745 grm., or 11.40 per cent in weight, the formula $C_{20}H_{24}N_2O_2 \cdot 2HCl + C_2H_6O$ requiring 10.38 per cent.

These lamellated crystals thus contained 1 molecule of alcohol. They have somewhat the appearance of those obtained from an aqueous solution, but which contained 2½ molecules of water. They have not, however, been observed previously. When exposed to the air they rapidly lose their alcohol of crystallisation, but at the same time take up moisture from the atmosphere; thus they change into the neutral hydrochlorate of quinine with 2½ molecules of water. Even in a bottle imperfectly closed with a cork they lose their alcohol fairly rapidly.

In a second series of experiments I crystallised the neutral hydrochlorate of quinine in ordinary absolute alcohol, that is to say in alcohol containing slight traces of water. I dissolved the hydrochlorate with heat in this so-called absolute alcohol without taking the precautions pointed out in the preceding experiments, that is to say without preventing contact with moist air.

The crystals deposited, after starting them by introducing a crystal containing 1 molecule of alcohol and 1 molecule of water of crystallisation, are similar to those described previously. After desiccation they gave the same loss already shown by M. Biscaro and myself.

I wished to make certain whether the alcohol they lose under the action of heat contains water; I therefore distilled them on a bath heated to 150° and collected the liquid in a tube containing anhydrous colourless sulphate of copper. The salt became blue on contact, thus showing the presence of a certain proportion of water. I further observed that the distillate contained alcohol; it was combustible in the air.

Thus it is established that the traces of water contained in ordinary absolute alcohol, and those that this same alcohol may take up from the air, are combined in the crystals of the neutral hydrochlorate of quinine deposited in the solution. The crystals thus obtained, dried at 37° in a dry atmosphere, lose one molecule of alcohol and half a molecule of water. They form a salt with half a molecule of water, which is stable in dry air. In moist air this salt takes up water, forming the salt with two and a-half molecules of water.

I have also effected the crystallisation of the neutral chlorhydrate of quinine by adding directly a very small quantity of water to the absolute alcohol used as a solvent. I first obtained the crystals containing one molecule of alcohol; then after starting the crystallisation of the mixture with a crystal containing one molecule of alcohol and one molecule of water, crystals containing the latter amounts of alcohol and water were deposited on the first-named.

This experiment leaves no doubt that we have here to deal with two different crystals.

The following is no less conclusive:—When to a crystallisation of the salt containing one molecule of alcohol, immersed in its own mother-liquor of absolute alcohol, we

add a very small quantity of water, and start the action by means of a crystal containing one molecule of alcohol and one molecule of water, the crystals containing one molecule of alcohol only gradually change into crystals containing one molecule of alcohol and one molecule of water; this is also easily observed by their change of appearance. When the proportion of alcohol to water is appropriate we are able to obtain both kinds of crystals simultaneously and directly.

I may add that the crystals containing one molecule of alcohol, when exposed to slightly moist air in a confined space, change their appearance; they become transparent rapidly and take all the characteristics of the crystals containing one molecule of alcohol and one molecule of water. —*Journ. de Pharm. et de Chim.*, Series 6, vol. xxii., No. 7.

THE DECOMPOSITION OF SULPHATE OF AMMONIUM BY HOT SULPHURIC ACID IN THE PRESENCE OF PLATINUM.

By MARCEL DELÉPINE.

I HAVE observed that the intervention of spongy platinum to regulate the boiling of sulphuric acid, as is done in the estimations of nitrogen by Kjeldahl's method, causes a heavy or the total loss of ammonia, and it appeared to me to be of interest to find out definitely the mechanism of this reaction, which has some connection with my old experiments on the insufficiency of Kjeldahl's method for the estimation of nitrogen in chloroplatinates (Delépine, *Bull. Soc. Chim.*, 1895, Series 3, xiii., p. 222).

These experiments were confirmed by W. van Dam in a more extended research (*Rev. Trav. Chim. P.-B.*, 1895, xiv., p. 217); this writer has further accepted my opinion put forward as a hypothesis, that the chloroplatinates brought about their own decomposition by a sort of internal dehydrogenation as follows:— $\text{PtCl}_6(\text{NH}_4)_2 + \text{Cl}_2 = \text{N}_2 + \text{PtCl}_4 + 8\text{HCl}$, the chlorine being furnished by the decomposition of the chloride of platinum; but without verifying it, he still imagined that the platinum-black deposited during the reaction played an active rôle; this supposition was based primarily on the fact that the chloroaurates did not cause any loss of nitrogen, although chloride of gold is as easily decomposed as chloride of platinum.

I would here mention that if we refer to the numerous estimations of nitrogen made by M. van Dam in various chloroplatinates with organic bases, we shall see that the addition of sulphate of potassium, according to Gunning's modification, causes greater losses of nitrogen than if we use sulphuric acid only; these losses may be even total. They are also very high if we have to heat for a long time in order to destroy the organic matter.

All these observations are fully explained by my new experiments.

If we boil sulphuric acid containing sulphate of ammonium, in the presence of spongy platinum or platinum-foil, we notice a loss of nitrogen which becomes greater as the experiment is prolonged, and, for the same time, that it takes place at a higher temperature; this is easy to regulate between 338° and 370° by adding from 0 to 50 per cent of sulphate of potassium to the sulphuric acid. If the amount of sulphate of ammonium is sufficient the platinum does not change appreciably in weight; the reaction thus has the character of those reactions called *catalytic*.

The nitrogen disappears in the form of gas (a fact already observed by M. van Dam). At the same time sulphurous acid gas is formed; thus it is only natural to think that the hydrogen of the ammonia is burnt by a portion of the oxygen of the sulphuric acid, according to the equation $2\text{SO}_4\text{H}(\text{NH}_4) + \text{SO}_4\text{H}_2$ or $\text{SO}_4(\text{NH}_4)_2 + 2\text{SO}_4\text{H}_2 = \text{N}_2 + 3\text{SO}_2 + 6\text{H}_2\text{O}$.

This equation was verified by a double series of experi-

ments. We introduced into sulphuric acid (both with and without SO_4K_2) in the presence of platinum, a known quantity of sulphate of ammonium; after the reaction we estimated the loss of nitrogen by difference while estimating the remaining ammonia. On the other hand, thanks to an arrangement easily fitted up, we were able either to collect the nitrogen directly, or to direct the sulphurous acid gas formed into a titrated solution of iodine, and by means of the above equation to calculate the loss of nitrogen corresponding to this gas. The results are very concordant, as is shown by the following figures:—

N from $\text{SO}_4(\text{NH}_4)_2$.	N lost according to the remaining ammonia.	Nitrogen collected.
0.0683	0.0287	0.0274
0.0713	0.0189	0.0193
0.0715	0.0340	0.0342
0.0431	0.0174	0.0179
0.0716	0.0559	0.0539
0.0711	0.0046	0.0044
0.0712	0.0102	0.0102
0.0681	0.0154	0.0160
0.0672	0.0258	0.0263

To make the speed of this destruction more clear, I will point out that in one hour 0.03 grm. of spongy platinum, from the calcination of chloroplatinate of aniline, caused a loss of 0.008 grm. of nitrogen in a mixture formed of 30 c.c. SO_4H_2 , 20 grms. SO_4K_2 , and 0.30 grm. $\text{SO}_4(\text{NH}_4)_2$; without the addition of potassic sulphate the loss is five or ten times less during the same time.

We may attempt to account for the above phenomena in two ways:—

1. Hot sulphuric acid in contact with platinum splits up into $\text{O} + \text{H}_2\text{O} + \text{SO}_2$, as at a higher temperature; the oxygen is not given off but combines with the hydrogen of the ammonia.*

2. Sulphuric acid attacks platinum and forms a sulphate, which is destroyed by the ammoniacal salt, regenerating the platinum:— $4\text{SO}_4\text{H}_2 + \text{Pt} = (\text{SO}_4)_2\text{Pt} + 2\text{SO}_2 + 4\text{H}_2\text{O}$, $3(\text{SO}_4)_2\text{Pt} + 2\text{SO}_4(\text{NH}_4)_2 = 2\text{N}_2 + 3\text{Pt} + 8\text{SO}_4\text{H}_2$.

The second process is the true one.

It can be proved that sulphuric acid attacks platinum almost at the speed it does silver; the coloured solution obtained deposits the greater portion of its platinum if we heat with sulphate of ammonium. We have, further, an indirect proof, in that spongy gold and iridium, which are not attacked by sulphuric acid, do not cause any loss of nitrogen if they are substituted for the platinum.

To sum up, platinum brings about the decomposition of sulphate of ammonium by boiling sulphuric acid, and should never be used in working Kjeldahl's method.

This decomposition takes place thanks to the momentary solution of the platinum. The attack of the platinum by sulphuric acid having been regarded as a controversial matter, or having been diversely interpreted, I have examined it specially in this paper.—*Bull. Soc. Chim.*, Series 3, vol. xxxv., No. 1.

Molecular Weight of Silver Vapour.—H. v. Wartenberg.—Using the apparatus devised by *Nernst* for determining vapour densities, and a modification of *Victor Meyer's* method, the author has determined the vapour density of silver. In nine experiments he found molecular weights varying from 107 to 147, thus showing that the vapour is monatomic in the neighbourhood of the boiling-point.—*Berichte*, xxxviii., No. 2.

* The opinion that boiling sulphuric acid splits up on contact with platinum into $\text{O} + \text{H}_2\text{O} + \text{SO}_2$ was offered as an explanation of this experiment by *Redwood* (*Pharm. Journ.*, [2], v., p. 602) that the distillation of sulphuric acid in a platinum retort gives a slightly weakened acid ($d = 1.842$ instead of 1.843), and with a sulphurous odour. Now, as *Redwood* added sulphate of ammonium before distilling, his observation bears on the facts I have observed, and which I interpret in Paragraph 2. When operating in glass retorts *Redwood* did not observe this phenomenon.

WET AND CRUCIBLE-FIRE METHODS FOR
THE ASSAY OF GOLD TELLURIDE ORES,
WITH NOTES ON THE
ERRORS OCCURRING IN THE OPERATIONS
OF FIRE ASSAY AND PARTING.*

By W. F. HILLEBRAND and E. T. ALLEN.

(Continued from p. 111).

PART II. THE ERRORS IN GOLD ASSAYING.

Cupellation Losses.

Absorption and Volatilisation.

THAT the loss of silver in assaying may be very marked is, of course, well known, particularly that loss which is due to too high heat during cupellation. That gold suffers similar losses, though to a much less degree, has been fairly well established by various workers. "That loss of gold takes place in cupellation if this is conducted at too high a temperature, or if the alloy is cupelled without quartation silver, is an already long known experimental fact" (Bodeman-Kerl's "Assaying," 1880, p. 194, translation by Goodyear). The data relating to gold are, however, not so satisfactory as those with respect to silver, and they are at times uncertain or even conflicting. It is in general said that the cupellation of gold may be carried out at a considerably higher temperature than that of silver, and the assayer is commonly advised to complete the final stage of the operation further back in the muffle than the earlier stages. Some authorities insist on the absence of feather litharge at the end. There seems to be in the literature no adequate appreciation of the very marked effect that slight differences in temperature actually do produce on the yield of gold by cupellation, especially if the ore be rich, nor of the very considerable volatilisation loss that accompanies cupel absorption if the heat is not kept at a minimum. Doubtless these facts are known to individual assayers, but they are not sufficiently emphasised in chemical literature, especially that to which practical assayers in this country usually have access. "Many yet believe that the degree of heat has little or no influence on the result" (Roessler in *Dingler's Polytech. Journ.*, 1872, ccvi., p. 186).

Our own experiments, which follow, were all made with proof gold and silver from the Mint. The results are not therefore necessarily comparable with those obtained by assaying ordinary bullion, where the presence of copper is said to demand a higher temperature, and to influence the gold loss.

First, gold alone was cupelled in order to ascertain primarily the loss with increase of temperature, and, secondarily, how this loss was affected by the amount of lead used. Ordinarily six cupels were set in a row, from front to back of the 12 by 6 inch muffle, so that the front cupel always showed at the end abundant feather litharge, and the rear one was at the back-end of the muffle. The cupellations were made in most cases with an altogether unnecessarily large amount of lead (25 grms.), in order to duplicate as nearly as might be the conditions under which the assays described in Part I. were cupelled. Table VIII. shows these results.

Then quartation mixtures were cupelled and the silver as well as the gold losses determined (Table IX.).

The foregoing tables show most strikingly the effect of increasing temperature on the loss of gold (and silver), and that this loss with pure gold is almost wholly by cupel absorption. A difference of position in the muffle amounting to no more than the width of a cupel is of great moment. The percentages given in the last two columns of Series A, Table VIII., and of Series B, Table IX., are of course subject to considerable probable error because of the difficulty of weighing such small beads to hundredths of a milligram, and the probability of losses

inherent in the operations by which they were obtained. Further, because of the probable retention of traces of lead by the large gold beads (see below, Experiment I.), the volatilisation figures are, if anything, too low and those for absorption too high.

It is clear that the following statements are far from correct:—

"A high temperature has no ill effect, the loss of gold in cupellation being so small that it need not be considered. It is about balanced by the silver left in the gold after parting. The cupellation loss is about 0.07 per cent" (Beringer, "A Text-book of Assaying," 1890, p. 128).

"The loss of gold by cupellation is insignificant (about 0.7 per 1000), compensated, moreover, by the small quantity of silver which the gold retains after parting (Campredon, "Guide Pratique du Chimiste Métallurgiste," 1898, p. 689).

"All the silver lost is absorbed by the cupel" (Campredon, *Ibid.*, p. 304).

Our experience goes to show that, as a general direction, the following should be modified, for with pure gold and telluride ores no higher heat is needed than for silver cupellation.

"A high heat is maintained throughout the operation [cupellation], and especially at the time of brightening; that is to say, a higher degree than is admissible in a silver assay . . ." (Aaron, "Assaying," 1900, p. 36).

The average loss named in the first two of these extracts is from three to seven times less than the lowest of those in Tables VIII. and IX.—those suffered at the lowest permissible limit of temperature.

Though not connected with the present discussion, it is impossible to see why the following, credited to Aidarow, should be true:—

"The gold, however, only soaks into the cupel when it has been scorified with lead beforehand. If gold is added to lead that is already fused on the cupel, no loss of gold takes place on cupellation" (Bodeman-Kerl, "Assaying," translated by Goodyear, 1880, p. 171).

That a small but appreciable portion of the total loss is due to volatilisation the results of Series A, Table VIII., and Series B, Table IX., clearly show. That such loss occurs is mentioned by some writers (Makins, *Quart. Journ. Chem. Soc.*, 1861, xiii., p. 97; Roessler in *Dingler's Polytech. Journ.*, 1872, ccvi., p. 189; Ricketts and Miller, "Notes on Assaying," 1897, pp. 128 and 129); but most writers make no mention of it. According to Rose ("Metallurgy of Gold," p. 479), 10 per cent of the total loss in bullion assay is by volatilisation, a proportion roughly agreeing with the returns in Table VIII., Series A, final columns.

That gold volatilises slowly if kept above its melting-point Napier has shown (*Quart. Journ. Chem. Soc.*, 1858, x., p. 229), but this condition does not ordinarily, if at all, obtain after the bead has brightened, so that the direction that it is quite safe to leave gold beads in the muffle after brightening for almost any length of time seemed probably justified. To test the point, however, a number of trials were made by cupelling several beads simultaneously and taking them out at intervals of one-half, five, and twenty minutes after pushing them back in the muffle to brighten. No constant losses were suffered by those left in for the longer periods, but curiously enough there seemed to be a slight tendency to increase in weight. To what this could be attributed is not clear.

On their face the results of Series C, Table VIII., as compared with Series B of the same table, seem to indicate that the amount of lead exerts a very marked effect on the gold loss. Roessler is fully persuaded from his own table of tests that this is generally true (*Dingler's Polytech. Journ.*, 1872, ccvi., p. 188). But compare for a moment the three series of Table IX. The same amount of lead was used in them all (25 grms.), and the absolute losses of gold with 30 m.grms., and with 10 m.grms. were practically identical, while with 15 m.grms. (Series B) they dropped to about one-third. Here the only seemingly probable explanation is that the temperature

* United States Geological Survey. *Bulletin* No. 253. (Series E, Chemistry and Physics, 44).

TABLE VIII.—*Losses of Gold when Cupelled without Silver as affected by Temperature and Amount of Lead.*
(25 grms. in Series A and B, 5 grms. in Series C).

	Gold taken. M.grms.	Gold found. M.grms.	Loss.		In cupels. M.grms.	Volatilised. M.grm.	Loss by absorption. Per cent.	Loss by volatilisation. Per cent.
			M.grm.	Per cent.				
Series A	1. 30'58	30'47	0'11	0'36	0'15	—	136	—
	2. 30'32	29'96	0'36	1'19	0'29	0'07	80	20
	3. 30'63	30'09	0'54	1'76	0'57	—	105	—
	4. 30'45	29'30	1'15	3'78	0'89	0'26	77	23
	5. 30'16	28'90	1'26	4'17	1'17	0'09	93	7
	6. 30'66	29'30	1'36	4'43	1'25	0'11	92	8
Series B	1. 10'34	10'31	0'03	0'29	—	—	—	—
	2. 10'25	9'77	0'48	4'68	—	—	—	—
	3. 10'29	10'15	0'14	1'36	Litharge formed faster than it could be absorbed during much of the time, yet the furnace ran at an unusually high heat.			
	4. 10'27	9'20	1'07	10'42				
	5. 10'17	8'56	1'67	16'43	—	—	—	—
	6. Lost	—	—	—	—	—	—	—
Series C	1. 10'36	10'33	0'03	0'29	5 grms. lead.			
	2. 10'31	10'23	0'08	0'78				
	3. 10'31	10'16	0'15	1'45				
	4. 10'17	9'87	0'30	2'95				
	5. 10'29	9'84	0'45	4'37				
	6. Lost	—	—	—				

TABLE IX.—*Losses of Gold and Silver when Cupelled together.*
(25 grms. Lead).

(25 grms. Lead).										In cupels.				Percentage of loss.				
Gold.		Gold loss.		Silver.		Silver loss.		Absorbed.		Volatilised.		Absorbed.		Volatilised.				
Taken.	Found.			Taken.	Found.			Au.	Ag.	Au.	Ag.	Au.	Ag.	Au.	Ag.			
M.grms.	M.grms.	M.grms.	Per cent.	M.grms.	M.grms.	M.grms.	Per cent.											
Series A.																		
1.	30·06	29·91	0·15	0·50	90·51	88·97	1·54	1·70										
2.	30·40	30·03	0·37	1·22	90·19	86·82	3·37	3·73										
3.	30·60	29·89	0·71	2·32	90·74	85·71	5·03	5·51										
4.	30·07	28·94	1·13	3·76	90·67	83·73	6·94	7·66										
5.	30·61	29·42	1·19	3·89	90·75	83·51	7·24	7·98										
6.	Lost	—	—	—	—	—	—	—										
Series B.																		
1.	15·56	15·53	0·03	0·19	45·06	44·20	0·86	1·91	0·02	0·70	0·01	0·16	67	81	33	19		
2.	15·14	15·08	0·06	0·40	45·19	43·70	1·49	3·30	0·05	1·17	0·01	0·32	83	78	17	22		
3.	15·15	14·92	0·23	1·52	45·41	43·53	1·88	4·14	0·12	1·19	0·11	0·69	52	63	48	37		
4.	15·44	15·12	0·32	2·07	45·30	42·68	2·62	5·78	0·22	1·63	0·10	0·99	67	62	33	38		
5.	15·52	15·12	0·40	2·59	45·59	42·61	2·98	6·55	0·27	2·09	0·13	0·89	67	70	33	30		
6.	15·39	15·02	0·37	2·40	45·05	42·07	2·98	6·61	0·27	2·13	0·10	0·85	73	71	27	29		
												Mean	..	..	68	71	32	29
Series C.																		
1.	10·67	10·62	0·05	0·47	30·33	29·67	0·66	2·17										
2.	10·57	10·40	0·17	1·61	30·64	28·90	1·74	5·68										
3.	10·53	9·99	0·54	5·13	30·42	27·32	3·10	10·19										
4.	10·63	9·50	1·13	10·63	30·52	25·64	4·88	15·99										
5.	10·60	9·28	1·32	12·46	30·38	24·81	5·57	18·34										
6.	10·21	8·93	1·28	12·53	30·44	24·75	5·69	18·69										

throughout the muffle must have been appreciably lower with B than with A and C. Hence it is not improbable that a similar explanation may be the proper one to adopt for the low results of Series C in Table VIII. The cause is certainly not conclusively shown, and it has been made plain that slight differences in temperature produce marked effects.

The final columns in Series B, Table IX., are of interest as showing that with quartation alloys not only is the volatilisation loss of gold greater than when pure gold is cupelled, but also that the ratio of volatilisation loss to absorption loss is about the same for both gold and silver, or, roughly, as 30 to 70. We regret that similar comparisons were not made for the other series. It is hoped

that at some future time opportunity may offer to test this and other points of interest more critically. For the present, however, this is impossible owing to the enforced abandonment of the survey's fire-assay laboratory. It is largely due to this latter fact that the work herein described is rather fragmentary and not altogether satisfying.

(To be continued).

Combination of the Rare Metals of the Cerium Group; their Sulphates in particular. — Camille Matignon.—The author claims priority over M. Otto Brill regarding a number of experiments on certain sulphates of the rare earths.—*Comptes Rendus*, cxlii., No. 7.

CONDENSATION COMPOUNDS OF CAMPHOR-
OXALIC ACID AND AMINES.*

SEVENTH COMMUNICATION ON CAMPHOROXALIC
DERIVATIVES.

By J. BISHOP TINGLE, Ph.D., F.C.S.,
and
WILLIAM EDWIN HOFFMAN, Jun., Ph.D.

(Continued from p. 113).

AMINE DERIVATIVES OF CAMPHOROXALIC ACID.

I. *β*-Naphthylamine.

1. *β*-Naphthylamine (6.4 grms. = 2 molecules) and camphoroxalic acid (5 grms. = 1 molecule) were mixed in boiling alcoholic solution, which was then kept at about 100° on a water-bath for a few minutes. Fine yellow needles soon began to separate out, and, on cooling, a mass of such crystals was deposited. The yield was almost quantitative. The compound is fairly readily soluble in hot alcohol, and is purified by re-crystallisation from it. The purified compound was deposited in the form of fine needles of a pale yellow colour and melted at 169° with the evolution of a gas. Analysis showed it to be *β*-naphthylamine *β*-naphthylcamphoformeneaminecarboxylate,—

0.1723 grm. substance gave 8.6 cc. N at 18° and 770 m.m.

Calculated for C_8H_{14}	$\begin{array}{c} \text{C} : \text{CCOONH}_3\text{C}_{10}\text{H}_7 \\ \\ \text{CO} \text{ NHC}_{10}\text{H}_7 \end{array}$	N.	..	5.66
Found				5.74

This salt when treated in alcoholic solution with ferric chloride did not give the violet-red colour characteristic of the enol grouping.

2. When the above compound is heated with a solution of sodium hydroxide, it dissolves, forming sodium *β*-naphthylcamphoformeneaminecarboxylate, and liberating *β*-naphthylamine, which is deposited on cooling the liquid, and was identified by its melting-point, 112°. On acidification of the solution of the sodium salt with dilute hydrochloric acid, the free *β*-naphthylcamphoformeneaminecarboxylic acid is precipitated. It was purified by re-crystallisation from benzene, and is deposited in yellow needles, melting at 172.5—173°. This corresponds to the melting-point obtained for the same compound which was prepared by J. Bishop Tingle (*Journ. Am. Chem. Soc.*, 1901, xxi., 375). The acid dissolves readily in sodium carbonate solution with the evolution of carbonic anhydride, and in alcoholic solution produces no red colour with ferric chloride.

3. When *β*-naphthylamine *β*-naphthylcamphoformeneaminecarboxylate is heated above its melting-point, it gives off a gas which was proved to be carbonic anhydride by the production of barium carbonate when it was led into a solution of barium hydroxide. A white solid sublimes into the upper part of the tube in which the fusion is being made, and by its melting-point was shown to be *β*-naphthylamine. The fused material, after the evolution of gas had ceased, is purified by means of alcohol, and crystallises in pale yellow needles melting at 173°. Analysis showed it to be *β*-naphthylcamphoformeneamine.

0.1783 grm. substance gave 7.1 c.c. N. at 12° and 760 m.m.

Calculated for C_8H_{14}	$\begin{array}{c} \text{C} : \text{CH} \\ \\ \text{CO} \text{ NHC}_{10}\text{H}_7 \end{array}$	N.	..	4.59
Found				4.73

With ferric chloride in alcoholic solution no violet-red colour was produced. When *β*-naphthylcamphoformene-

aminecarboxylic acid is heated above its melting-point it gives off carbonic anhydride, and forms a compound melting at 173°, identical with that formed from the *β*-naphthylamine *β*-naphthylcamphoformeneaminecarboxylate by heating.

II. *Paratoluidine*.

1. Camphoroxalic acid (5 grms. = 1 molecule) and paratoluidine (4.8 grms. = 2 molecules) were mixed in boiling alcoholic solution, which, on cooling, deposited a mass of fine yellow needles. The yield seemed to be nearly quantitative. The compound is soluble in alcohol, and is purified by re-crystallisation from it. The purified compound crystallises in slender yellow needles, and melts at 152° with the evolution of a gas. With ferric chloride in alcoholic solution it gave no colour reaction. Analysis proved it to be *paratoluidine paratolylcamphoformeneaminecarboxylate*.

0.1818 grm. substance gave 10.2 c.c. N at 13° and 765 m.m.

Calculated for C_8H_{14}	$\begin{array}{c} \text{C} : \text{CCOONH}_3\text{C}_6\text{H}_4\text{CH}_3 \\ \\ \text{CO} \text{ NHC}_6\text{H}_4\text{CH}_3 \end{array}$	N.	..	6.66
Found				6.67

2. When the above compound is heated with sodium hydroxide solution it dissolves, forming sodium *paratolylcamphoformeneaminecarboxylate*, which, on acidification with dilute hydrochloric acid, precipitates the free *paratolylcamphoformeneaminecarboxylic acid*; this is insoluble in water, and forms a pale yellow mass. The substance, after re-crystallisation from benzene, is deposited in yellow needles, and melts at 168° with the evolution of a gas. It dissolves in sodium carbonate solution with the liberation of carbonic anhydride, and with an alcoholic solution of ferric chloride produces no colour. Analysis showed it to be *paratolylcamphoformeneaminecarboxylic acid*.

0.1605 grm. substance gave 6.2 c.c. N at 6° and 770 m.m.

Calculated for C_8H_{14}	$\begin{array}{c} \text{C} : \text{CCOOH} \\ \\ \text{CO} \text{ NHC}_6\text{H}_4\text{CH}_3 \end{array}$	N.	..	4.47
Found				4.64

3. When the *paratoluidine paratolylcamphoformeneaminecarboxylate* is heated above its melting-point it gives off a gas which was proved to be carbonic anhydride by the production of barium carbonate, when it was led into a solution of barium hydroxide. When the tube in which the fusion is being made is allowed to cool, a white crystalline solid appears in its upper part; this by its melting-point, 42.5°, was demonstrated to be *paratoluidine*. The fused material, after the evolution of gas had ceased, was re-crystallised from alcohol, and is deposited in very pale yellow crystals melting at 178°. With alcoholic ferric chloride no colour is produced. Analysis showed it to be *paratolylcamphoformeneamine*.

0.1710 grm. substance gave 7.8 c.c. N at 12° and 755 m.m.

Calculated for C_8H_{14}	$\begin{array}{c} \text{C} : \text{CH} \\ \\ \text{CO} \text{ NHC}_6\text{H}_4\text{CH}_3 \end{array}$	N.	..	5.20
Found				5.37

When *paratolylcamphoformeneaminecarboxylic acid* is heated above its melting-point it gives off carbonic anhydride, and forms a compound melting at 178°, identical with the one just described, which is formed by heating the *paratoluidine* salt of this acid.

* From the *American Chemical Journal*, xxxiv., No. 3.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 1st, 1906.

Mr. A. G. VERNON HARCOURT, F.R.S., Past President, in the Chair.

MESSRS. A. T. Braid, H. E. Fierz, W. P. Hayworth, H. A. D. Neville, F. W. Walker, E. Wechsler, and J. L. White were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edwin Rodney Chrystall, Forest Villa, Prince's Road, Buckhurst Hill, Essex; Robert K. Duncan, University of Kansas, U.S.A.; Ernest Feilmann, B.Sc., Ph.D., F.I.C., 2A, Dartmouth Road, Brondesbury, N.W.; James Louis Foucar, B.Sc., 20, St. John's Park, Blackheath, S.E.; Richard John Hall, M.Sc., F.I.C., "Sandy-croft," Serpentine Road, Egrement, Liverpool; Walter Daly Scouller, B.Sc., 7, Stamp Office Place, Wakefield; James Frederick Spencer, M.Sc., Ph.D., 134, Rice Lane, Walton, Liverpool; Francis W. Storey, B.Sc., 42, Ellerdale Street, Lewisham, S.E.; George Augustus Turner, Alma House, Strandtown, Belfast.

A certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Hem Chandra Dutt Gupta, "Guptanibar," Krishnagar, Bengal, India.

Of the following papers, those marked * were read:—

* 45. "Studies of Dynamic Isomerism. Part IV. Stereoisomeric Halogen Derivatives of Camphor." By THOMAS MARTIN LOWRY.

Measurements were given of the solubility in alcohol of α -chloro- and α -bromo-camphors, α 3- and $\alpha\pi$ -dibromo-camphors, and $\alpha\beta$ - and $\alpha\pi$ -chlorobromocamphors, both alone and in presence of a small proportion of sodium ethoxide. In each case it was found that the addition of alkali resulted in an increase of solubility in the ratio of about 0.9 to 1. No such increase was observed in the case of β -bromocamphor, or of compounds in which both the α - and α' -hydrogen atoms were displaced. The increase of solubility is ascribed to the formation in the solution of a small proportion (7 to 12 per cent) of the stereoisomeric α' -compound (compare Kipping, *Proc.*, 1905, xxi., 124 and 125).

* 46. "The Coagulating Action of Colloids." (Part I.) By WILLIAM PORTER DREAPER and ALEXANDER WILSON.

The addition of tannic acid to an organic colloid like gelatin or albumin in the hydrosol state determines the amount of gallic acid absorbed by the coagulum. The gallic acid may be present before or after the addition of tannic acid. Acids like hydrochloric or acetic reduce this absorption. Salts, on the other hand, increase it. These acids do not seem to replace the gallic acid by mass action or otherwise.

Gelatin in the hydrogel state absorbs gallic acid, although no precipitation takes place if the former is in the hydrosol state. Salts increase absorption, but alcohol reduces it.

Albumin absorbs gallic acid when precipitated by either tannic acid or heat. Alcohol prevents this action and also the absorption of tannic acid by albumin. Addition of gallic acid to a "solution" containing tannic acid and albumin causes rapid coagulation. This reaction is dependent on concentration. In very concentrated solutions, gallic acid will precipitate albumin.

Absorption by silk is greatly reduced in presence of alcohol, the tannic acid absorbed is reduced from 15 to 1.2 per cent. Hide powder behaves in a similar way, the tannic acid absorbed being reduced from 72 to 10 per cent. Solutions of gelatin, "collin," and albumin give these reactions.

The results obtained by the author throw further light on dyeing and tanning processes. The influence of gallic acid

in the manufacture of leather seems to be of a more direct nature than was previously supposed.

DISCUSSION.

Mr. DREAPER, in reply to questions from Dr. Cain, stated that "collin" was a form of soluble gelatin used by Parker and Payne in the estimation of tannic acid; it did not enter the hydrogel state at the ordinary temperature.

The tannic and gallic acids were estimated by the process he had suggested some time ago. The tannic acid was titrated with copper sulphate solution in the presence of calcium carbonate. The separation of the two acids was brought about by precipitating the former as lead tannate in the presence of a definite excess of acetic acid, which prevented the gallate being precipitated at the same time. The gallic acid in the filtrate was then estimated as copper salt.

* 47. "Studies on Optically Active Carbimides. III. The Resolution of α -Phenyl- α' -4-hydroxyphenylethane by means of *l*-menthylcarbimide." By ROBERT HOWSON PICKARD and WILLIAM OSWALD LITTLEBURY.

A method of resolving racemic hydroxyl compounds by means of *l*-menthylcarbimide was described. The *l*-menthyl-carbamates thus obtained by the combination of these compounds can be separated by fractional crystallisation and are then hydrolysed by alcoholic sodium hydroxide. *d*- α -Phenyl- α' -4-hydroxyphenylethane *l*-menthylcarbamate separates in a pure condition from light petroleum and melts at 117°. When hydrolysed, it yields *d*- α -phenyl- α' -4-hydroxyphenylethane, which melts at 64° and has $[\alpha]_D + 7.78^\circ$ in benzene.

DISCUSSION.

Dr. A. MCKENZIE asked whether the authors had obtained any evidence of the partial resolution of an inactive phenol into its optical isomerides by the action of an amount of *l*-menthylcarbimide insufficient for complete interaction. A partial resolution might be expected to occur under such conditions if the velocity of interaction of the *d*-phenol with the *l*-carbimide were different from that of the *l*-phenol. That an inactive alcohol may be partially resolved into its optical isomerides has been shown with *sec*-octyl alcohol (*Ber.*, 1901, xxxiv., 474).

It would be interesting to know whether the temperature conditions under which the fractional crystallisation described by the authors took place had much influence on the progress of the resolution.

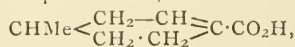
Dr. PICKARD, in reply to a question from Dr. Forster, stated that the method of obtaining carbimides by the action of nitrous acid on the corresponding carbamides could not be used for the preparation of *l*-menthylcarbimide, as this reacts too readily with water.

In reply to Dr. McKenzie, he said that in attempting the resolution of α -phenyl- α' -4-hydroxyphenylethane by treatment with half its equivalent of *l*-menthylcarbimide, some experimental difficulties supervened and led to the adoption of the easier method of fractionally crystallising a mixture of the two modifications of the *l*-menthyl-carbamates. No evidence of a transition temperature was observed during the investigation.

* 48. "Experiments on the Synthesis of the Terpenes. Part VIII. Synthesis of the Optically Active Modifications of Δ^3 -*p*-menthenol(8) and Δ^3 : δ (9)-*p*-menthadiene." By FRANCIS WILLIAM KAY and WILLIAM HENRY PERKIN, jun.

The terpenes and their derivatives, which have so far been obtained synthetically (*Trans.*, 1904, lxxxv., 654; 1905, lxxxvii., 639, 655, 661, 1067, and 1083; *Proc.*, 1905, xxi., 255), have always been inactive, but the following optically active members belonging to this group have now been synthesised.

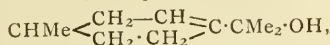
Δ^1 -Tetrahydro-*p*-toluic acid,—



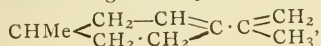
contains an asymmetric carbon atom, and by the systematic

crystallisation of its brucine and strychnine salts the authors have resolved it into its dextro- and levo-modifications. The levo-modification obtained from the brucine salt has a rotation of $[\alpha]_D - 100^\circ$, whereas the dextro-acid obtained from the strychnine salt has a corresponding rotation of $[\alpha]_D + 101^\circ$.

The esters of these acids were prepared by the action of alcoholic sulphuric acid; ethyl d- Δ^1 -tetrahydro-p-toluate boiled at $154^\circ/100$ m.m. and had $[\alpha]_D + 86^\circ$, the levo-modification boiled at $154^\circ/100$ m.m. and had $[\alpha]_D - 84^\circ$. On treating the latter with the theoretical amount of magnesium methyl iodide and then decomposing with water and dilute acid, l- Δ^3 -p-menthenol (8),—



was obtained; this substance boils at $101^\circ/14$ m.m. and has $[\alpha]_D - 67^\circ$. When this menthenol is digested with potassium hydrogen sulphate, partial racemisation takes place, and the resulting $\Delta^3 : 8(9)$ -p-menthadiene,—



which distils at $185^\circ/748$ m.m., has a rotation $[\alpha]_D$ of only -10° .

Pure d- $\Delta^3 : 8(9)$ -p-menthadiene was, however, obtained by the direct action of excess of magnesium methyl iodide on the d-ester without the aid of the acid sulphate; it boils at $184-186^\circ/756$ m.m. and has $[\alpha]_D + 98^\circ$. The magnetic rotations and other physical constants of these interesting substances are being determined.

*49. "Studies in the Acridine Series. III. The Methylation of Chrysanthine." By ALBERT ERNEST DUNSTAN and JOHN THEODORE HEWITT.

The authors have continued the research on the lines laid down by Hewitt and Fox (*Trans.*, 1904, lxxxv., 529, and 1905, lxxxvii., 1058), and have prepared the diacetyl and tetra-acetyl derivatives of chrysanthine, starting from the purified base.

By treatment with methyl iodide and methyl alcohol, the diacetyl derivative afforded an acridinium methiodide, which on hydrolysis immediately gave an anhydro-base; this substance was also prepared by the use of methyl sulphate and subsequent hydrolysis and precipitation with ammonia.

50. "Note on the Application of the Electrolytic Method to the Estimation of Arsenic in Wall Papers, Fabrics, &c." By THOMAS EDWARD THORPE.

Known quantities of the material, as a rule about 2 grms., are moistened with lime water, mixed with calcined magnesias, dried, and charred. The ash is treated with dilute sulphuric acid, half a gm. of potassium metabisulphite added, the solution boiled and diluted to a definite volume, and the whole or an aliquot portion, depending on the amount of arsenic suspected to be present, is added to the electrolytic arrangement already described (*Trans.*, 1903, lxxviii., 974). The deposit of arsenic so obtained is then compared with deposits obtained in precisely the same way by the addition of known quantities of arsenic, ranging from 0.005 to 0.0125 milligram of arsenious oxide, to materials free from arsenic, as in the method of testing brewing materials for arsenic already described (*loc. cit.*). A single incineration of the suspected material suffices for several tests. The amounts of lime-water and magnesia recommended to be used have been proved by direct experiment to retain amounts of arsenic ranging from 0.0025 to 5 milligrams when contained in 2 grms. of wool or paper.

Many samples of woollen materials met with in commerce contain very notable quantities of arsenic, arising probably from the widespread use of arsenical dips.

51. "Nitrogen Halides from Camphoryl- ψ -carbamide." By MARTIN ONSLOW FORSTER and HANS GROSSMAN.

The action of potassium hypobromite and hypochlorite on camphoryl- ψ -carbamide has been found to give rise to dihalogen derivatives which have all the properties of com-

pounds containing halogen attached to nitrogen. Normal camphorylcarbamide yields the same substances, owing to the readiness with which it changes into the *pseudo*-modification under the influence of alkalis. Corresponding monohalogen derivatives have been obtained from camphoryl-methyl- ψ -carbamide and its normal modification.

52. "The Relation of Position Isomerism to Optical Activity. VI. The Rotation of the Menthyl Esters of the Isomeric Chloronitrobenzoic Acids." By JULIUS BEHREND COHEN and HENRY PERCY ARMES.

It was pointed out in a previous paper on this subject (*Trans.*, 1905, lxxxvii., 1192), that whereas chlorine and bromine atoms in the ortho-position to the active group lower its rotation, the nitro-group has the opposite effect of greatly increasing it. In the present investigation, the combined effect of halogen and nitro-group on the activity of the menthyl group has been examined. The authors have studied the rotations of eight out of the ten isomeric chloronitrobenzoic esters, the 2-chloro-3-nitro- and 3-chloro-2-nitro compounds being omitted owing to difficulties of preparation.

Annual General Meeting.

The Annual General Meeting of the Society for the election of Officers and Council and other business will be held on Friday, March 30th, 1906, at 5 o'clock in the afternoon.

The PRESIDENT will deliver his address entitled "The Living Organism as a Chemical Agency: A review of some of the Problems of Photosynthesis by Growing Plants."

SOCIETY OF CHEMICAL INDUSTRY (LONDON SECTION).

Ordinary Meeting, March 5th, 1906.

Mr. A. G. SALAMON in the Chair.

"The Ignition of Nitro-compound Explosives in Small Arm Cartridges." By W. D. BORLAND.

The action of the igniter, i.e., the percussion cap, is to eject through the fire-holes of the case a mixture of solid and gaseous products at temperatures between 2400° C. and 3200° C. in such quantity, volume, and time that the initial resistance of the bullet or shot is overcome before the bulk of the charge of powder develops its full energy, but without any hesitation which may upset alignment or perceptible "hang fire." The rapidity with which these gaseous and solid matters are applied to the powder is determined by exploding the percussion cap in a hollow steel cylinder provided with a hardened steel plunger, and resting upon a crusher lead. The proportion which the crushing pressure bears to total energy is found in practice to be a trustworthy guide to the rapidity with which the heat of the igniter is applied to the explosive, and consequently to the ratio which chamber pressures in the small arm bear to observed velocity of projectile.

The volume of the gaseous matters in relation to the surface of the explosive can be readily determined. These must be large enough to ensure sufficiently high chamber pressures being set up for the most efficient combustion of the powder.

The temperature of ignition was determined by radiation methods of observation, the cap being exploded into a glass tube and the radiation intensity of the solids observed by comparison with a radiant of known intensity, the portion of the spectrum chosen being in the neighbourhood of 6563 wave-length.

The paper includes tables illustrating the action of different igniters on different explosives, both sporting and military, and tracing the effect of total heat energy and temperature of igniter upon velocity, pressure, and rapidity of ignition observed in ballistic trials.

NOTICES OF BOOKS.

Experimental Electrochemistry. By N. MONROE HOPKINS, Ph.D. London: Archibald Constable and Co., Ltd. 1905.

THIS book displays considerable originality in many respects, and teachers of electrochemistry will undoubtedly be able to gather useful hints from it. It is intended to be used both as a theoretical text-book and as a practical laboratory guide, and it is for the latter purpose that it will probably be most appreciated. The descriptions of the various experiments are clear and explicit, and should serve to inculcate a careful spirit in the worker, who is duly warned of the importance of paying attention to those minutiae of practice which are sometimes overlooked. Although the practical notes and hints are particularly valuable, the more theoretical parts of the subject are very satisfactorily treated, the discussion and defence of the theory of electrolytic dissociation being specially worthy of remark, while another valuable feature is the provision of suggestions for additional experiments and for research work, which are introduced at various stages throughout the book. The range of subjects treated is wide, and they are selected in such a way as to make the reader familiar with almost all the important and fundamental work that has been done in most branches of electrochemistry; chapters on the electric furnace, on the preparation of organic compounds, and on the production of nitric acid from the atmosphere being included. The diagrams are clear, and no difficulty should be experienced in setting up the apparatus with their assistance.

Les Erreurs de la Science. ("The Errors of Science"). By LOUIS CHARLES EMILE VIAL. Paris: The Author. 1905.

IT has been left to the author of this work to discover that the hypotheses of science are all false, and that its facts are wrongly interpreted, and to propound a new theory of the universe. The author's earlier works, of which this book is an amplification, have met with the reception which, judging from this specimen, they fully deserve, and the author has yet to learn that sincere convictions and a profound belief in his own achievements are not the only equipment necessary for the successful writer of a criticism of the whole region of natural and moral science. It would be profitless to discuss the theories put forward and the supposed results obtained, and it is difficult to believe that even those whom curiosity impels to open the book will be able to read more than a few pages before throwing it aside, thoroughly exasperated by the errors of judgment, the exaggerations and false reasoning displayed in it.

Über die Oxydation des Stickstoffs in der Hochspannungsflamme. ("The Oxidation of Nitrogen in the High Potential Flame"). By Dr. Phil. JOHANNES BRODE. Halle-a-S.: Wilhelm Knapp. 1905.

THIS monograph on the oxidation of nitrogen at a very high temperature discusses the theory of the process, and summarises the work which has been done on the subject from the time of the first experiments of Bunsen and Kolbe, performed when they were investigating the products of the explosion of detonating gas and the consequent fixing of nitrogen, to the present day. The researches of Muthmann, Hofer, and Nernst are very fully described, and publications dealing with the oxidation of nitrogen, both by means of chemical reactions and by the electric discharge, are carefully abstracted. The second half of the monograph is devoted to the discussion of the author's own experiments carried out during the years 1904-1905 at the Institute of Physical Chemistry and Electrochemistry attached to the Technical High School at Karlsruhe. The most suitable means for producing the flame, and the

dependence of the concentration of the nitric oxide formed upon various factors are described in this part of the book, the results obtained by making alterations in the material of the electrodes, their distance apart, the strength of the current, moisture, temperature, &c., being considered at some length.

L'Année Electrique. ("The Electrical Year"). By Dr. FOVEAU DE COURMELLES. Paris: Ch. Béranger. 1906.

THIS annual review of electrical progress is chiefly occupied with the practical applications of the science, special attention being paid to the employment of electrical methods in medicine, though other branches are not altogether neglected. Electrotherapeutics and radiography fill a good portion of the volume, which gives a very readable review of advances made in the year 1905. A great defect in the book is the total absence of all references to original papers, a list of which would double its value. The various articles are, generally speaking, abstracted without comment, and no information is given as to where the original was published for the benefit of those who want further details.

CORRESPONDENCE

THE ANALYSIS OF DOLOMITE.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS of December 1, 1905 (vol. xcii., p. 259), Messrs. Clowes and Coleman express their disagreement with our methods described in a previous communication as to the estimation of certain constituents of dolomite (CHEMICAL NEWS, vol. xcii., p. 108). We would say that we have further experimented with the estimation of silica in dolomites, limestones, siderites, and some other minerals, and we have found that, as a rule, either no silica or an inappreciable amount goes into solution after dissolving in hydrochloric acid. At any rate, an evaporation of the hydrochloric acid filtrate does not yield silica, and if there is any in solution it would be necessary to seek it in a later stage of the analysis in connection with iron and alumina. The results of our experiments will be published at some future time.

With regard to the value of (A), a double precipitation of iron and alumina, as against (B), the single precipitation, we obtain the following results:—

	(A). Double precipitation. Per cent.	(B). Single precipitation. Per cent.
1.	0.56	0.59
2.	—	0.545

and with a second specimen—

	0.47	0.49
1.	0.47	0.49
2.	—	0.47

We still maintain that if one is careful to use only a small excess of ammonium hydrate in the precipitation, even though the ammonia contains some ammonium carbonate, a double precipitation is not necessary. It is unnecessary to add more than a drop or two in excess, as the iron present serves as a perfect indicator. The very small amount of calcium carbonate thus precipitated would doubtless be removed by properly washing the precipitate.

Messrs. Clowes and Coleman obtained in a certain specimen of dolomite 1.43 per cent of iron and alumina by the single precipitation, and 1.35 per cent by the double precipitation. They infer that 0.08 per cent of calcium is precipitated in the first instance. That seems like a rather small difference to obtain by two distinct methods, especially in view of the fact that it is not easy to obtain exactly concordant results by the same method.

A competent authority (Washington, "Rock Analysis") says:—"No method is capable of yielding results of absolute accuracy." If one were to make determinations of iron in the same specimen, for example, by permanganate or bichromate titration, would he not be satisfied with results that varied from one another by within 0.1 per cent?

A method of estimating carbon dioxide in a mineral or rock is described in a well-known and valuable work (Crookes, "Select Methods," p. 600), where it is claimed that by using 5 grms. of Iceland spar the method will give 43.97 per cent of carbon dioxide, 44 per cent being the theoretical.

The degree of concordance of course depends on the nature of the analysis. Results of the analyses of organic substances by combustion are often published when they differ by 0.30 per cent to 0.50 per cent from one another, or from the theoretical. An authority suggests (Washington, "Rock Analysis"), if in the analysis of a rock the sum of the constituents found aggregate from 99.50 per cent to 100.75 per cent, the results can be accepted as satisfactory.

Can it be certain that a sample of rock is usually mixed so thoroughly that two portions from the same would be exactly identical? If this could be assumed, the set of weights used would have to be very finely calibrated to give identical results. Then there looms up the possibility that the distilled water may not be perfect, and the reagents employed may not be absolutely pure, and even if they are all that could be desired, they might attack the glass, all of which works against perfect results. If, therefore, Messrs. Clowes and Coleman obtain results by two different methods that vary by only 0.08 per cent, would it not be an argument in favour of the simpler and easier method?

Concerning the importance of removing the ammonium salts before precipitating the magnesium, Hillebrand (*Bull. U.S. Geol. Survey*, p. 64) says:—"It is not necessary to first remove ammoniacal salts unless very little magnesium is present, and then only to hasten precipitation." Newbauer (*Zeit. für Angew. Chem.*, 1896, p. 435) has shown that precipitation is complete, even in presence of large quantities of salts of ammonium, including the oxalate. Messrs. Clowes and Coleman also generously admit that "the difference in the percentage of MgO is not so important."

The writer acknowledges his indebtedness to Mr. A. A. Wells for assistance in the experimental work before described.—I am, &c.,

NICHOLAS KNIGHT.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 7, February 12, 1906.

Re-combination of Ions of Saline Vapours.—G. Moreau.—On account of the value of their mobility, as well as their coefficient α , the ions of saline vapours between the temperatures of 170° and 0° lie between the ions of ordinary gases and the total ions due to the oxidation of phosphorus. In proportion as the temperature rises their mass diminishes, and when heated in a flame these ions become comparable with particular cathodic particles for the negative ion, and the atom of hydrogen for the positive ion.

Calcium Iodomercurates.—A. Duboin.—A saturated solution of mercury iodide in calcium iodide when filtered is of density 2.89, and has a composition represented by the formula $\text{CaI}_2, 1.30\text{HgI}_2, 12.3\text{H}_2\text{O}$. When left to cool, a deposit of very voluminous yellow crystals comes down,

which are extremely deliquescent, and correspond to the formula $\text{CaI}_2, \text{HgI}_2, 8\text{H}_2\text{O}$, and have density 3.258 to 3.337. A second iodomercurate may be obtained from the same solution in the form of very small crystals, and having formula $\text{CaI}_2, 5\text{HgI}_2, 8\text{H}_2\text{O}$. A third one, by cooling the solution below 0°, appears in the form of long prisms having formula $3\text{CaI}_2, 4\text{HgI}_2, 24\text{H}_2\text{O}$ and density 3.56 to 3.66.

Phosphorus Sulphides.—H. Giran.—The existence of a certain number of phosphorus sulphides is still under discussion. An investigation of the temperature of fusion of mixtures of varying proportions of sulphur and phosphorus enables the author to make some definite statements on this subject. His researches are all made on mixtures which were previously heated to a higher temperature, and in which there was certainly a union of the two non-metals. He finds that mixtures of sulphur and phosphorus, which are liquid at ordinary temperatures, show very markedly the phenomenon of surfusion.

Preparation and Properties of Strontium.—MM. Guntz and Roederer.—The authors prepare strontium in the same manner as M. Guntz previously prepared barium. First, strontium hydride is prepared quite free from mercury by the action of hydrogen on strontium amalgam. In the vacuum of a mercury pump, at about 1000°, this compound dissociates, and the strontium vapour can then easily be condensed on a cold steel tube. The properties of this substance, which contains 99.43 per cent of pure strontium, are then examined.

Action of certain Bibasic Acid Ethers on the Halogen-magnesium Derivatives of the Primary Aromatic Amines.—F. Bodroux.—The author previously showed that neutral ethyl carbonate reacts on the halogen-magnesium derivatives of the primary aromatic amines, giving rise to the mono-substituted derivatives of urethane. If neutral ethyl oxalate is used, a symmetric disubstituted oxamide is produced, and with excess of the ethyl oxalate a very small quantity of substituted oxamic ether is formed, $\text{CO}-\text{NH}-\text{R}$.

The author obtains, with good yields, COOC_2H_5 diphenyloxamide, ortho- and para-dicresyloxamides, and with a bad yield, β -dinaphthyloxamide.

Constitution of Chromic Sulphates.—Albert Colson.—The green sulphate resulting from the reduction of a cold solution of chromic acid by means of sulphur dioxide has for its composition after desiccation in a vacuum $\text{Cr}_2(\text{SO}_4)_3 + 7.5\text{H}_2\text{O}$. It contains two concealed SO_4 radicals, and is transformed into a turquoise-blue salt, $\text{Cr}_2(\text{SO}_4)_3 + 10\text{H}_2\text{O}$, which contains only one concealed radical. These two bodies are intermediate between the ordinary violet sulphate, of which the entire acid acts on barium chloride, and a unknown sulphate of which the acid is entirely concealed, and of which the author in this present research establishes the existence.

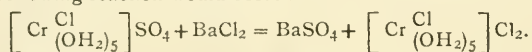
Existence of Bicarbonates in Mineral Waters, and supposed Anomalies in their Osmotic Pressures.—L. C. Maillard and Lucien Graux.—The authors calculate individually the part which each of the constituents of a mineral water plays in the establishment of the osmotic pressure, and they find that, in the cases examined, the cryoscopic results offer no opposition to the admitted notion of the existence of bicarbonates in the waters. Further, a judicious application of the laws of cryoscopy to mineral waters dispels the supposed anomalies of the osmotic pressure.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 2, 1906.

Autoxidation of Trivalent Titanium.—W. Manchot and P. Richter.—If caustic potash is added to a salt of trivalent titanium and the precipitate of titanium sesquioxide obtained is shaken up with oxygen, oxidation proceeds

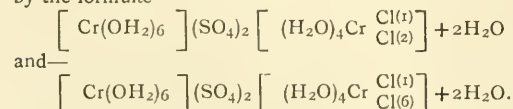
takes place, a considerably greater volume being absorbed than corresponds to one equivalent of oxygen. On being acidified the solution becomes yellow. Hydrogen peroxide first results, but it is again partially reduced by the titanous oxide, and forms pertitanic acid only on acidifying, or possibly even in the alkaline liquid. To explain this process by a quantitative experiment it was first of all necessary to prevent the secondary action of the hydrogen peroxide in the alkaline liquid. This was done by using a fairly thick paste of lime instead of caustic potash. A solution of titanium sesquioxide was prepared by reducing a sulphuric acid titanium dioxide solution with zinc. A hydrochloric acid solution, produced by the action of barium chloride upon the sulphuric acid solution could also be employed. These solutions rapidly undergo a change in air, but may be kept for some time in a flask filled with hydrogen. Due precautions were taken to prevent the oxidation of the titanium before mixing with alkali, and the end of the oxidation was recognised by the complete decoloration of the precipitate. It was found that all the oxygen taken up was quantitatively converted into hydrogen peroxide. The latter is totally precipitated by the lime. Not only is the action of the hydrogen peroxide on the unoxidised titanium hindered by the lime, but also the formation of pertitanic acid cannot result under these conditions until after acidification; *i.e.*, secondarily. The direct formation of TiO_3 would require the absorption of three equivalents of oxygen.

Chromium Salts.—A. Werner and R. Huber.—Recoura has described a chlorosulphate of chromium to which he gave the formula $[Cr^{Cl}_{(OH)_5}]SO_4 + 1H_2O$. The authors hoped that when this was treated with barium chloride the following reaction would occur:—



They found, however, that under these circumstances a green solution was obtained, which after concentration gave the original chlorosulphate on addition of sulphuric acid, but when they tried to obtain the supposed new chloride, $[Cr^{Cl}_{(OH)_5}]Cl_2$, in the pure state they found that it was not a single compound, but a mixture of green and blue chromium chlorhydrate. Hence they supposed that Recoura's chlorosulphate contained a hexaquo-chrom complex, and this assumption was confirmed as follows:—If the chlorosulphate was exposed to moist air upon a clay plate for some time, its blue-green colour altered, and finally a reddish violet powder consisting of violet chromium sulphate remained behind. Hence it must be concluded that Recoura's chlorosulphate has not the simple formula, but it is probably a di-molecular compound

$Cr(OH)_6 \begin{smallmatrix} SO_4 \\ SO_4 \end{smallmatrix} [Cr^{Cl_2(OH)_2}_2]$. This assumption may be proved synthetically by adding concentrated sulphuric acid drop by drop to an ice-cold mixture of concentrated solutions of violet chromium sulphate and green chromium chloride, $[Cr^{Cl_2}_{(OH)_4}]Cl + 2H_2O$. A copious precipitate of green crystals is obtained which have the same composition as Recoura's chlorosulphate and behave similarly, but there are certain differences in the crystalline form and colour of the two compounds. Possibly these differences may be explained by assuming a spacial difference in the complexes of the two salts, $[Cr^{Cl_2}_{(OH)_4}]$, as represented by the formulæ—



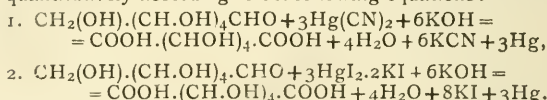
This assumption must be accepted with caution, and it is important to note that neither Recoura's chlorosulphate

nor the synthetic compound gives a precipitate of silver chloride when silver nitrate is added to the freshly prepared neutral aqueous solution.

Aldehydes as Acids.—H. Euler.—It has been shown that formaldehyde is a weak acid, whose dissociation constant amounts to $1 \cdot 10^{-14}$ at 0° , and that with alkalis it forms salts which are half hydrolysed in normal solution. The author has examined other aldehydes—chloral hydrate, *d*-fructose, *d*-glucose, acetaldehyde, and furfural—and finds that they all behave like acids, their dissociation constants being $4 \cdot 10^{-12}$, $3 \cdot 6 \cdot 10^{-13}$, $1 \cdot 8 \cdot 10^{-13}$, $0 \cdot 7 \cdot 10^{-14}$, and less than $1 \cdot 10^{-16}$ respectively. In all probability the formation of salts is a general property of aldehydes, though it cannot always be detected by the means at present at our disposal.

Oxidation of Trivalent Titanium (II).—W. Manchot and P. Richter.—Trivalent titanium behaves like divalent iron when oxidised by molecular oxygen, requiring twice as many equivalents as correspond to the conversion of Ti_2O_3 into $2TiO_2$, but in the case of iron no hydrogen peroxide is formed. Iron exhibits the same peculiarity towards other oxidisers, *e.g.*, chromic acid and permanganic acid. If a solution of chromic acid and hydriodic acid is prepared and a titanium sesquioxide solution added, iodine is liberated, and may be determined by titration with thiosulphate. The experiments show that two equivalents of iodine are liberated, so that altogether three equivalents of oxygen are replaced by one atom of titanium. With permanganate the same result is obtained. If reduced titanium solution is added to a mixture of permanganate and hydrochloric acid, of such strength that it changes only very slowly, a strong smell of chlorine is noticed.

Two New Methods for the Quantitative Determination of Grape-sugar.—B. Glassmann.—1. *Indirect Volumetric Method.*—When glucose is oxidised by means of an alkaline mercury cyanide solution, or a mercury iodide-potassium iodide solution, the oxidation proceeds quantitatively according to the following equations:—



Measured quantities of a grape-sugar solution of known strength are introduced into excess of boiling alkaline mercuric cyanide solution, and the mercury is filtered off, dissolved by heating with concentrated nitric acid, and the mercury in the nitrate thus obtained is determined by Rupp and Krauss' method; *i.e.*, the solution is diluted with water, saturated iron alum solution and nitric acid added, and the mixture titrated with rhodammonium in the usual way till a permanent light brown coloration is obtained.

2. *Gas Volumetric Method.* If mercury cyanide or mercury iodide-potassium iodide is warmed with a hydrazine salt the following reaction occurs quantitatively:—



If the nitrogen is collected, the amount of mercury in the mercury solution can be calculated from it. If a grape-sugar solution is treated with a known excess of titrated mercury cyanide solution by Method 1 and the excess of mercury is determined by treating the alkaline solution with excess of hydrazine sulphate, the difference gives the mercury separated by the oxidation of the grape-sugar, and from this the strength of the grape-sugar solution can be calculated (3 grms. Hg = 1 molecule $C_6H_{12}O_6$).

Action of Atmospheric Oxygen upon Paracautchouc.—Edgar Herbst.—A solution of purified paracautchouc in benzene was heated for one hundred and forty hours, and treated with atmospheric air which had been freed from dust and moisture, the benzene which evaporated being replaced. During the process the originally colourless solution gradually became yellower and yellower. At the end of the operation a small quantity

of a yellowish grey resinous substance had collected on the bottom of the flask and in the tube through which the air was introduced. This substance was apparently not soluble in alcohol, petroleum ether, glacial acetic acid, or carbon disulphide, but there was not enough of it for a further examination. The benzene solution when filtered off gave no precipitate of caoutchouc on addition of alcohol. When the benzene was evaporated, a syrupy transparent reddish brown mass remained behind. This when treated with petroleum ether went into solution for the most part, leaving a small greyish yellow residue. The petroleum ether solution on evaporation left a perfectly clear syrup of light reddish brown colour and a peculiar aromatic smell. Its composition corresponded to the formula $C_{10}H_{16}O$. The resinous substance, insoluble in petroleum ether, was re-precipitated from benzene solution with petroleum ether, and then yielded an amorphous mass with a faint aromatic odour. Analysis showed that its composition was $C_{10}H_{16}O_3$. The liquids from which this compound, richer in oxygen, was precipitated were collected and evaporated. After repeated precipitation from benzene solution by means of a large excess of petroleum ether, a greasy substance was obtained of empirical formula $C_{10}H_{16}O_3$. It formed a hard mass *in vacuo*. The oxidation product, $C_{10}H_{16}O_2$, could not be prepared.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, March 20, at 5 o'clock, Mr. J. E. Marr delivers the first of three lectures at the Royal Institution on "The Influence of Geology on Scenery" (the Tyndall Lectures); and on Thursday, March 28, at the same hour, Prof. Bertram Hopkinson begins a course of three lectures on "Internal Combustion Engines" (with Experimental Illustrations). The Friday Evening Discourse on March 23 will be delivered by Lord Roberts on "Imperial Defence"; on March 30 by Prof. Zeeman, on "Recent Progress in Magneto-optics"; and on April 6 by Mr. W. B. Hardy, on "The Physical Basis of Life."

Thermoelectric Properties of Alloys.—N. N. Tournour.—The author has examined the thermoelectric properties of alloys of tin with bismuth and lead, of lead with bismuth, and of some alloys of copper with zinc. The electromotive force was measured relatively to copper; one of the junctions was kept at 0°, the other at 100°. He found:—1. That the electromotive force of alloys of tin and lead is constant, and does not depend upon the composition of the alloy; it is the same as that of lead. 2. The electromotive force of alloys of bismuth with tin and lead, and of copper with zinc, varies in amount and even in direction according to the proportion of the components. 3. The maximum electromotive force corresponds with alloys which appear to be definite compounds, $SnBi_5$ and $PbBi_3$. 4. Alloys of lead and bismuth, of copper and zinc, and of zinc and lead are examples of phases in which the electromotive force remains constant and independent of the composition; for example, with lead and bismuth at 65 per cent of lead and over, with copper and zinc between 10 per cent and 25 per cent of zinc. 5. The alloys of copper and zinc have at least two maxima and two minima, so that by varying the composition the direction of the current changes at least four times. The numerical values have not yet been confirmed. 6. With time there is produced in the alloys of bismuth with tin or lead a modification which manifests itself by a diminution of the electromotive force.—*Journ. Soc. Phys. Chim. R.*, vol. xxxvi., p. 1119.

The Halogen Salts of Palladium.—A. Gutbier and A. Krell.—The chloropalladites and the chloropalladates

of the alkaline metals are anhydrous, and their formulæ are respectively $PdCl_4M_2$ and $PdCl_6M_2$; the same is the case with the corresponding bromides. The chloro- and bromopalladates are decomposed by boiling water with the disengagement of chlorine or bromine; the same action takes place with concentrated sulphuric acid. They are also reduced by ammonia with the disengagement of nitrogen. *Chloropalladite of Ammonium*.—We evaporate carefully the mixture $PdCl_2 + 2NH_4Cl$; beautiful yellowish green needles are formed, soluble in water, giving a deep brownish red colour. *Chloropalladite of Cesium*, bright brown precipitate, re-crystallises in warm water in the form of needles. *Chloropalladate of Cesium*, a brownish yellow precipitate almost insoluble in cold water, resulting from the action of chlorine on a solution of chloropalladite. *Chloropalladite of Rubidium* resembles the cesium salt, re-crystallises in the form of silky needles. *Chloropalladate of Rubidium*, an orange coloured microcrystalline precipitate resembling the cesium salt. *Bromopalladite of Ammonium* is obtained in the same way as the double chloride; beautiful reddish brown needles, very soluble even in the cold. *Bromopalladate of Ammonium*.—We cause the vapour of bromine to act slowly on a cold solution of the preceding salt; it forms regular black octahedra, very slightly soluble. *Bromopalladite of Cesium*, reddish brown needles, very soluble. *Bromopalladate of Cesium*, precipitate of black octahedra, prepared in the same manner as the salt of ammonium. *Bromopalladite and Bromopalladate of Rubidium* resemble the corresponding cesium salts. *Bromopalladate of Potassium*, beautiful black octahedra, soluble in cold water, giving a brown coloration.—*Berichte*, vol. xxxviii., p. 2385.

Products of the Higher Oxidation of Chromium.—E. H. Riesenfeld, H. E. Wohlers, and W. A. Kutsch.—The authors have prepared afresh the salts obtained by Hoffmann and Hiendlmaier, and give them the formula CrO_8M_3 instead of CrO_6M_2 . The salt of ammonium, $CrO_8(NH_4)_3$, is prepared by cooling to below 0° a solution of 50 c.c. NH_3 at 25 per cent, and 25 c.c. of CrO_3 at 50 per cent; to 75 c.c. we then add carefully 25 c.c. of H_2O_2 at 30 per cent, and prevent the temperature rising above 0°. The liquid becomes brown, and after a few hours deposits crystals, which are drained and washed several times with alcohol at 95 per cent. In a similar manner the salts of potassium and sodium are prepared. If, on the other hand, we operate in an acid solution, we obtain the blue salts of M. Wiede (for example, for the ammonium salt, $CrO_7H_2NH_4$ we take 100 c.c. of water, 5 c.c. of concentrated HCl , 10 grms. of NH_4Cl , 50 c.c. CrO_3 , and 25 c.c. of H_2O_2 at 30 per cent), only the washing with alcohol should be rapid on account of the solubility of the blue salts. The salts of ammonium or potassium, (CrO_8M_3), form small reddish brown irregular octahedra; the sodium salt occurs in orange-coloured plates. These salts do not undergo any change in absolute alcohol or anhydrous ether even when boiling. If these liquids contain water there may be some change with the formation of aldehyde. Cold water dissolves them slightly, but it decomposes them slowly. Neutral or alkaline solutions soon form chromates and oxygen, which solutions, strongly acidulated with sulphuric acid, form, first of all, perchromic acid, then a chromic salt. The well-dried salts keep better in a slightly moist atmosphere (almost indefinitely, in fact); the sodic salt is the one that undergoes spontaneous decomposition most rapidly. Finally, heat alone decomposes the salt of potassium at about 170° into KOH , CrO_4K_2 , and oxygen. The presence of impurities makes the salts more easily decomposable by heat, sometimes even explosive. When moistened with concentrated sulphuric acid the salts deflagrate, throwing off in all directions green morsels of Cr_2O_3 . The same phenomenon takes place by submitting the salt of ammonium to a shock; there is, further, a violent explosion. The salts of potassium and sodium are insensible to shock.—*Berichte*, vol. xxxviii., p. 1885.

MEETINGS FOR THE WEEK.

- MONDAY, 19th.—Society of Arts, 8. (Cantor Lectures). "Fire, Fire Risks, and Fire Extinction," by Vivian B. Lewes.
- TUESDAY, 20th.—Royal Institution, 5. (Tyndall Lectures). "The Influence of Geology on Scenery," by John E. Marr, F.R.S., &c.
- Society of Arts, 8. "English Royal Heraldry," by Cyril Davenport, F.S.A.
- WEDNESDAY, 21st.—Microscopical, 8. "Contribution to our Knowledge of the Rotifera of South Africa," by C. F. Rousselet. "Resolving Limits for the Telescope and the Microscope," by E. M. Nelson.
- Society of Arts, 8. "Motor Boats," by B. B. Redwood, B.A.
- THURSDAY, 22nd.—Royal Institution, 5. "Internal Combustion Engines" (with Experimental Illustrations), by Prof. Bertram Hopkinson, M.A., &c.
- FRIDAY, 23rd.—Royal Institution, 9. "Imperial Defence," by The Rt. Hon. Earl Roberts, V.C., &c.
- Physical, 5. "Unilateral Electric Conductivity over Damp Surfaces," by F. T. Trouton. "Construction and Use of Oscillating Valves for Rectifying High-frequency Electric Currents," by J. A. Fleming. "Use of the Cymometer for the Determination of Resonance Curves," by G. B. Dyke.
- SATURDAY, 24th.—Royal Institution, 3. "The Corpuscular Theory of Matter," by Prof. J. J. Thomson, F.R.S., &c.

WHARF at RAINHAM.—FREEHOLD.—River frontage to Rainham Creek, near the River Thames, and in the midst of the Industrial Factory district. With possession.

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THE CHEMICAL NEWS.

VOL. XCIII., No. 2417.

ROOT-SAP ACIDITY.

By W. F. SUTHERST, Ph.D., F.I.C.

A STANDARD solution to represent the dissolving power of root-sap on mineral matter would be an ideal implement in the hands of agricultural chemists, since, by its help, the amount of plant food in the soil and available matter in mineral manures could be determined with exactitude.

Certain English and foreign chemists have suggested solutions—notably Stutzer, Dehérain, Wagner, Dyer, Hughes, and others—such being based more or less on the acidity of root-sap, and containing either an organic acid or acid salt. It is obvious that there is an acid solution in the roots of all plants, and such would, of course, have a fairly strong solvent action on insoluble phosphates, chalk, potash compounds, &c., found in the soil, and one would expect that the roots containing the larger amounts of acid

contains about the largest percentage of mineral matter (viz., 2.04); while white clover, with an acidity of 1.43 per cent. contains only 1.43 per cent mineral matter. Phosphoric acid, present of course in the soil as insoluble bicalcium or other phosphates, is supposed to be particularly affected by the amount of acid in root-sap; but we see that rye grass, with its low root acidity, takes up slightly more than white clover. One might say that these plants for their growth need only a fixed amount of phosphoric acid, and take up but that quantity; but, during the evolution of these plants, if they in pre-historic times contained such acid sap, they would probably have adapted themselves to the larger quantities of phosphoric acid that they were capable of extracting out of the soil.

Since there is an acid liquid in the roots of all plants, it is probable that plant growing in very chalky soils would be affected by the neutralising action of the chalk, and some experiments were carried out here by me by growing wheat in soils containing various quantities of chalk, the crops being examined when grown for shoots, roots (in green and dry state), root-sap acidity, and mineral matter. The results obtained are given in Table II., the same number of seeds being used in each case.

The first thing noticeable is the diminished yield on the soil rich in chalk, then the amount of roots remaining practically constant; but the increasing proportion of roots

TABLE I.

	Water.	Root acid.	Root-sap acidity.	Ash.	P ₂ O ₅ .	K ₂ O.	Acid : Ash.
Rye grass	70	0.25	0.35	2.04	0.22	0.71	1 : 5.83
Potato (tops) ..	80.3	0.29	0.34	1.97	0.16	0.44	1 : 5.80
Pea	81.5	0.30	0.34	1.39	0.15	0.52	1 : 4.09
Sugar-beet	89.7	0.41	0.48	1.53	0.07	0.40	1 : 3.18
Timothy	70.4	0.50	0.80	2.05	0.24	0.70	1 : 2.56
Turnip (white) ..	89.8	0.46	0.51	1.19	0.08	0.28	1 : 2.33
Spinach	90.3	0.62	0.70	1.60	0.16	0.27	1 : 2.28
Oat	81.0	0.43	0.65	1.42	0.13	0.56	1 : 2.18
Onion	86.0	0.41	0.45	0.80	0.14	0.25	1 : 1.77
Celery	84.0	0.93	1.10	1.76	0.22	0.76	1 : 1.60
Cabbage	87.1	0.70	1.00	1.40	0.21	0.39	1 : 1.40
Artichoke	81.1	0.56	0.76	1.01	0.39	0.24	1 : 1.35
Red clover	82.0	1.10	1.37	1.55	0.13	0.55	1 : 1.13
White clover ..	80.5	1.00	1.43	1.43	0.18	0.31	1 : 1
Incarnate clover ..	81.5	0.83	1.28	1.13	0.08	0.26	1 : 0.88

TABLE II.

	Chalk in soil.	Shoots.	Roots.	Dry shoots.	Dry roots.	Roots to shoots.	Roots to shoots (dry).	Sap acidity.	Ash in dry matter.
	Per cent.	Grms.	Grms.	Grms.	Grms.				Per cent.
1.	1.30	146.5	99	24.7	16.8	1 : 1.48	1 : 1.41	0.295	12.77
2.	11.26	131	94.7	19.6	13.6	1 : 1.38	1 : 1.25	0.282	9.54
3.	21.40	109.7	95.0	17.3	15.7	1 : 1.15	1 : 1.13	0.260	7.14

would absorb more mineral matter (the elaborate analyses of Dyer on the acidity of root-sap proved that the amounts of acid in various plants varied considerably), but such is not the case, and is one drawback to using standard solutions based on the acidity of root-sap. On comparing the sap acidity of several plants with the amount of mineral matter they contain, it will be seen that the proportion is the reverse, viz., that the most acid roots bring less mineral matter into the plants. The flow of water through the plant system, due to transpiration, might have some effect in this case, but the amount of water transpired by the plants enumerated in Table I. is about the same, consequently some other reason must be given for this phenomenon. Table I. gives the plant, amount of water in same, amount of acid in the roots (expressed as citric acid), sap acidity—i.e., ratio of root acid to amount of water in roots (these figures taken from Dyer's "Available Mineral Plant Food in Soils"),—ash, phosphoric acid, potash, and proportion of acid to ash. It will be seen from this table that rye grass, with a weak root-sap acidity of 0.35 per cent,

to shoots show that the roots must have been travelling away from the plant base in their search for food, and probably endeavouring to avoid the chalk, for the roots of Nos. 2 and 3 were very much longer than No. 1. The root-sap shows a slight decrease in acidity, due no doubt to the neutralising action of the chalk. In testing the acidity, great care was taken to wash the root free from chalk, and no roots were tested without the washings were quite free from all trace of milkiness. After drying the roots, they were ground to a fine powder and the acid extracted by boiling water and titrated with normal alkali. The small amount of ash in the Nos. 2 and 3 samples also shows the neutralising action of the chalk, as the roots, having absorbed their requisite amount of lime, would most probably cease dissolving out mineral matter, which would be largely lime salts, and the plant cannot show a preference for one mineral substance—such as phosphate—when another is present in overwhelming quantities. Possibly the roots form a crust of calcium oxalate and tartrate when in contact with large quantities of chalk

which prevents the passage of moisture from without and acid sap from within; consequently the roots, in their search for food, try to leave the chalky region.

The Agricultural College, Tamworth.

NOTE ON THE PREPARATION OF BENZONITRILE.

By J. BISHOP TINGLE, Johns Hopkins University.

IN the course of some work which was being carried out in this laboratory in 1904, it was necessary to provide rather large quantities of benzonitrile; at my suggestion, therefore, Messrs. E. J. Hoffmann and W. A. Syme studied some of the various methods which have been proposed for the preparation of this compound. Their results are recorded in the following table; they have been checked in most cases by other students. The figures given for the cost are believed to be accurate *relatively*, the *absolute* cost is necessarily variable. In reckoning the time no account was taken of the washing and distillation of the crude product, as this was practically the same in all cases; the time required to dry an ethereal solution, when this was needful, has also been disregarded, because it did not occupy the worker. The yield refers to material which has been distilled.

Method I.—Sandemeyer's reaction (*Ber.*, xvii., 2653):—Aniline, 35 grms.; copper sulphate crystals, 100 grms.; potassium cyanide, 110 grms.; sodium nitrite, 25 grms.; and hydrochloric acid, 50 grms. were employed.

Method II.—From benzamide, 15 grms.; and phosphoric anhydride, 25 grms. (Hofmann and Buckton, *Ann. Chem. Pharm.*, c., 155).

Method III.—From benzoic acid, 100 grms.; and lead thiocyanate, 240 grms. (Krüss, *Ber.*, xvii., 1766).

Method IV.—From sodium benzenesulphonate, 100 grms.; and potassium cyanide, 100 grms. (Merz, *Ibid.*, iii., 710).

Method V.—From benzamide, 23 grms.; and quicklime in excess (Anschutz and Schulz, *Ann. Chem. Pharm.*, xcvi., 48).

Method VI.—From benzoic acid, 50 grms.; and potassium thiocyanate, 20 grms. (Letts, *Ber.*, v., 673).

As was to be expected Mr. Syme did not obtain a large yield of benzonitrile by the use of iodobenzene and silver cyanide (Merz and Weith, *Ibid.*, x., 746), nor was he able to get satisfactory results by the distillation of aniline oxalate (A. W. Hofmann (*Comptes Rendus*, lxiv., 388). He prepared benzamide very easily and quickly from benzoic acid and ammonium thiocyanate (Kekulé, *Ber.*, vi., 113).

Method.	Yields. Grms. the theoretical.	Per cent of	Time.	Cost of 100 grms.
I.	25	64	About 4 hours	0.72 dols.
II.	12	95	" 1 "	1.00 "
III.	60	71	" 10 "	0.55 "
IV.	15	26	" 1 "	5.86 "
V.	8.2	42	" 1 "	1.70 "
VI.	12.2	58	" 3 "	1.15 "

—*American Chemical Journal*, xxxv., No. 1.

Researches in the Pyrane Series.—E. E. Blaise and H. Gault.—To obtain pyranic homologues, the authors condense oxalacetic ether with various aldehydes, both cyclic and acyclic. The cyclic aldehydes do not give the alcoylidene-bisoxalacetic ethers, but only ketoarylparaconic ethers, on account of the elimination of 1 mol. of alcohol between 1 mol. of aldehyde and a single molecule of oxal-

acetic ether, $\text{CO} \begin{array}{c} \diagup \text{CH} \text{---} \text{CO}_2\text{C}_2\text{H}_5 \\ \diagdown \text{O} \text{---} \text{CH} \text{---} \text{C}_6\text{H}_5\text{---} \text{R} \end{array}$ By effecting the

condensation by means of gaseous hydrochloric acid, keto-paraconic ethers are obtained directly; if, on the contrary, diethylamine is employed, the corresponding salts of diethylamine are formed.—*Comptes Rendus*, cxlii., No. 8.

COMPARISON OF A WET AND CRUCIBLE-FIRE METHODS FOR THE ASSAY OF GOLD TELLURIDE ORES, WITH NOTES ON THE ERRORS OCCURRING IN THE OPERATIONS OF FIRE ASSAY AND PARTING.*

By W. F. HILLEBRAND and E. T. ALLEN.

(Concluded from p. 122).

PART II. THE ERRORS IN GOLD ASSAYING (*continued*).

Retention of Lead by Cupelled Beads,

INASMUCH as in hardly a single case did our corrected assays on proof metal show more than was weighed at the start, even at the lowest heat, with full feather litharge, it did not seem necessary to assume the presence of lead in the beads obtained. Nevertheless, in one case a number of them from the same series of assays were dissolved in aqua regia together, the gold precipitated, and the solution evaporated to a few drops. By exercise of the utmost care it was possible to detect a minute quantity of lead, too small, perhaps, to have influenced the results to any appreciable extent.

Later, the following experiments were carried out:—

Experiment 1.—Three beads of proof gold, weighing, respectively, 30.14, 50.40, and 10.35 m.grms., were cupelled with 2 grms. of lead each, in the ordinary way, and weighed after boiling with dilute hydrochloric acid to remove any film of lead oxide or particles of litharge-soaked bone-ash. They were then dissolved together in aqua regia, evaporated, diluted with sulphurous acid, the solution filtered, and evaporated till fumes appeared. The residue, consisting of lead sulphate and a little metallic gold, was transferred to a filter after taking up with alcohol, the sulphate extracted by ammonium acetate, the lead re-precipitated by hydrogen sulphide, re-converted into sulphate, and weighed. The weight was 0.0004 gm., equivalent to 0.3 per cent of lead.

Experiment 2.—Three beads of very nearly the same weights as those first acted on were treated in a similar manner, except that they were left in a muffle twenty minutes after brightening. The amount of lead recovered from all three together was 0.37 per cent.

This shows clearly, as had our earlier experience, that the error, though of some magnitude, is not lessened by leaving the beads in the muffle for a considerable time after brightening. It should be said that the sulphate weighed was certainly of lead and not silver. The percentages above given are, however, to be regarded as approximate only.

Losses of Gold in Slags.

From a statement in Fulton's paper, "Assay on Telluride Ores" (*Fourn. Am. Chem. Soc.*, 1898, xx., p. 589), we were led to expect much greater losses of gold in the slag than appear from the tables in Part I. of this paper. Fulton says that these are much greater with Cripple Creek telluride ores than with ordinary gold ores. They appear, however, so far as our own work goes, to be slight. We have suggested a possible explanation for his higher losses. (See "Discussion of Results," p. 109).

Errors in Parting.

Strength of Acid.

Most diverse is the practice in parting as to the strengths of acid employed. Vauquelin seems to have first used acid of 1.16 and 1.26 specific gravity, and these are the strengths most frequently recommended to-day. But there are not wanting those who prescribe other strengths, or who reverse the order of application—that is, employ the stronger acid first—or who are content with acid of uniform strength.

* United States Geological Survey. *Bulletin* No. 253. (Series E, Chemistry and Physics, 44).

Incomplete Extraction of Silver.

Not less diverse are the statements as to the completeness of the silver extraction. Campredon puts the average silver retention for bullion assay, tested upon an aggregate of 100 cornets, at 0.0002 grm. According to Beringer, the surcharge may amount to 0.05 per cent ("A Text-book of Assaying, 1890, p. 129). In Brown's "Assaying" (p. 396) it is said that "A small amount of silver will always remain in the cornet, no matter how carefully the manipulations may have been conducted." On the other hand, Ricketts and Miller say that the inaccuracy due to silver retention in parting can be avoided by careful work ("Notes on Assaying," 1897, p. 109). Later, however, they say (p. 128) with respect to gold bullion, "On the other hand, the gold always contains some silver and occluded gases." That cornets retain occluded gases was proved by Graham (*Phil. Trans. Roy. Soc.*, 1866, p. 433), and Varrentrapp showed that the amount varies with the temperature of annealing (Rose, "Metallurgy of Gold," p. 481).

Our own experience in the present work is that while sometimes by dissolving a number of beads together traces of silver were detected, quite as often none were found. This was before we learned the need for more than two or three boilings with acid. We believe that some of the unfavourable results reported by various writers may have been due to insufficient treatment with acid and inadequate washing. Not infrequently the direction is given to wash three times with water. That this is insufficient for such cornets as are obtained in bullion assay our own tests have proved to us. (See further).

There is great lack of agreement, too, as to the best gold-silver ratio in the quartation alloy. For instance, Chaudet and Kandelhardt are credited in "Bodeman-Kerl" (Goodyear's translation, 1900, p. 183) with the statement that a gold-silver alloy with 2½ parts of silver retains less silver when parted with nitric acid than an alloy with 3 parts. The same authority attributes to Pettenkofer the statement that the separation can succeed well with as little as 1½ parts of silver to 1 of gold. Rammelsberg (*Ibid.*, p. 184) is quoted to the effect that pure nitric acid dissolves all the silver out of an alloy containing 80 per cent and more of silver, and leaves all the gold behind; and, on the contrary, the separation is imperfect with a proportion of from 15 to 80 per cent of silver.

Impurities in Acid.

Of course, if the acid used for parting contains certain impurities, losses will occur. The impurity most to be guarded against is hydrochloric acid or chlorine. "Bodeman-Kerl" (Goodyear's translation, 1900, p. 187) mention also sulphuric and sulphurous acids. Rose ("Metallurgy of Gold," p. 479) ascribes, on the basis of his own tests, 8 per cent of the total loss in a gold assay to the solvent action of the acid, without specifying further. Lenher (*Journ. Am. Chem. Soc.*, 1904, xxvi., p. 552) confirms the statements of several authors as to the solubility of gold in a hot mixture of strong sulphuric and nitric acids, and that on dilution with water it precipitates, this precipitation being supposedly brought about by nitrous acid formed from the nitric acid. He also shows that the sulphuric-nitric acid mixture dissolves gold even at 0° C.

(Lenher in that paper gives interesting data on the solvent action on gold of a number of bodies other than the halogens, but they are outside the present discussion).

Action of Nitrous Acid.

The statement, which, according to Makins, can be traced to Berzelius, is met with in several places, that loss of gold ensues in parting from the solvent action of nitrous acid; and Makins (*Quart. Journ. Chem. Soc.*, 1861, xiii., p. 99), by repeated boilings of assay gold with nitric acid of specific gravity 1.25 and 1.35, was able to establish a steady loss which he attributed to nitrous acid, though the proof is by no means convincing, as he

does not clearly show the entire absence of traces of hydrochloric acid in his nitric acid, nor of silver in his cornets, nor did he evaporate the filtrates and prove that they contained gold. The active agent could not be nitrous acid formed from the solution of the quartation silver, for its formation must have practically ceased after the second or third boiling. Van Liew obtained astonishing results (*Eng. and Min. Journ.*, lxix., p. 498). He condensed nitrous acid, which he prepared by reducing potassium nitrate with lead and treating the nitrite with sulphuric acid, in a 30 per cent solution of nitric acid in which had been placed leaf-gold. At 15° C. about 1 to 2 per cent of the gold was found to have dissolved, and upward of 38 per cent at 82° C., and 51.9 per cent at an undetermined lower temperature.

In order to obtain light on this point one of us prepared nitrous acid, and tested its effect on spongy gold. Cold aqueous solutions were obtained by the method of Lunge from starch and nitric acid.

Experiment 1.—Twenty-five c.c. of the solution, containing 0.032 grm. HNO₂ and 0.401 grm. HNO₃ per c.c., was placed, in a pressure bottle with very thoroughly washed spongy gold, and left in contact for thirty-six hours, the final temperature being about 30°. Evaporation of the filtrate to dryness showed a small yellowish white residue, which proved to be mostly organic (a blank test gave the same result). When this was heated to redness a faint purple stain remained. This, when dissolved in a few drops of aqua regia and tested with stannous chloride, showed a trace of gold.

Experiment 2.—The solution was more concentrated, holding 0.0548 grm. HNO₂ and 0.075 grm. HNO₃ per c.c. A trace of gold was found.

Experiments 3 and 4.—In each of these 10 c.c. of solution containing 0.062 grm. of HNO₂ and 0.219 grm. of HNO₃ per c.c., was sealed in a tube with spongy gold, and heated for seven hours at about 150°. No gold was found in either case.

It is difficult to see how the above conditions can have differed materially from those in Van Liew's experiments; nevertheless, nitrous acid was made from pure potassium nitrate, and its action on spongy gold observed at a temperature of about 70° to 80° in pressure bottles. No solution of gold could be proved.

In all of the above experiments the acid was filtered through a close plug of ignited asbestos before testing for gold.

The results of these severe tests show that solvent action by nitrous acid during an assay need not be considered. The reported precipitating action of nitrous acid in dilute solution (see above) seems to be in direct opposition to such solvent action. Van Liew's abnormal results must have been due to using a nitrate containing chloride as the source of his nitrous acid.

Action of Nitric Acid.

To test the possible effect of nitric acid itself the following experiments were made:—

Four portions of pure gold were cupelled with three times their weight of silver and 5 grms. of lead each. Five boilings with acid, with intervening washings, were needed to extract the silver to such an extent that an ordinary test failed to show it longer in the extracts. Then No. 1 was boiled with 20 c.c. HNO₃ for fifteen minutes, washed, annealed, and weighed. No. 2 was boiled two periods of fifteen minutes each with acid and properly washed, then annealed, and weighed. With Nos. 3 and 4 the boiling with acid was repeated two and three times respectively, the duration of acid treatment in case of No. 4 lasting between one and two hours. The following table shows that no systematic losses appear, and that in the most severe test no loss whatever occurred. (See table, next column).

The acid thus used was tested for gold as follows:—It was evaporated in clean porcelain dishes, the residues were moistened with a few drops of water and wiped out

	Taken. M.grms.	Found. M.grms.	Loss. M.grm.
1	250'27	249'99	-0'28
2	250'23	250'29	+0'06
3	250'57	250'53	-0'04
4	250'38	250'38	—

clean with small pieces of filter-paper; these were wrapped in lead cornets to which a tiny piece of silver was added, cupelled, and parted.

No. 1 gave no gold. (The absence of gold here shows that the large apparent loss in weight of the cornet, as shown by No. 1 of the table above, was not due to solution of gold).

No. 2 gave 0.01 m.grm. gold.

No. 3 gave 0.01 m.grm. gold.

No. 4 gave no gold.

The acid used for parting was also carefully tested for gold after first precipitating the silver. That from the first four partings combined gave no gold. That from the second gave 0.02 m.grm. gold in all. This gold may have been float gold, though the utmost care was taken to guard against this source of error.

From the above it is plain that the losses in parting with pure acid, whether traces of gold really dissolve or not, are negligible in an ore assay at least.

In conclusion, it may be said that the gold beads, after the repeated treatments with nitric acid detailed above, were dissolved in aqua regia, and the solutions tested for silver with the greatest care, both before removal of the gold and afterwards. In not a single case could the slightest trace of silver be detected.

Summary of Results.

Not all of the conclusions here summarised are to be regarded as fully established, while some are but confirmations of earlier statements by others. More work is needed along certain lines, for there is more than one obscure point connected with the fire assay that needs greater attention than we were able to give it. To what extent the results for cupel losses by different workers will be influenced by a difference in the quality of the cupels used there is, unfortunately, no means of determining. The possibility of such a disturbing influence must always be borne in mind.

It is clearly established that the fire assay by crucible for gold telluride ores gives results which are quite equal to those obtained by the wet way, provided due corrections are made for slag and cupel losses.

The gold loss in the slag is very small, and generally negligible with the charge used by us,* but the cupel losses are very appreciable, and considering the far greater value of gold than of silver, weight for weight, it may be doubted whether the statement that "the loss of gold in the assay of any ore, except when extremely rich, is too small to require correction" (Ricketts and Miller, p. 110) is justified when very exact work is called for. Much depends on what is meant by "extremely rich." Doubtless the ores treated of in Part I. fall within this category, but the losses are there so detectable that correction seems called for with ores far less rich. In view of the very appreciable errors that always occur, and which it is quite impossible to wholly allow for in any ordinary assay, it seems that those who demand an assay balance weighing to less than the hundredth of a milligram are decidedly straining at a gnat if they are willing to swallow the camel of an uncorrected assay.

The cupellation loss of gold by volatilisation is generally small as compared with that by absorption, and at a temperature allowing the formation of abundant feather

litharge is negligible, or perhaps compensated by retention of lead (Table IV.), but the case is otherwise at high temperatures (Tables VIII. and IX.), when it may average one-half of that by absorption in the case of a quartation alloy. The results of Table VI. seem to contradict the first statement, for they show a much greater apparent loss by volatilisation than by absorption.

The loss of gold by absorption is a very important one, and is influenced, far more than is generally supposed, by slight changes in temperature. It is greater with pure gold and alloys poor in silver than with alloys rich in silver.

From a limited number of tests it appears that the ratio of volatilisation loss to absorption loss for quartation alloys at higher than the normal temperature of cupellation is about the same for both gold and silver, or roughly, 30 to 70. This point needs further testing.

Our experiments failed absolutely to show the need for a higher temperature at the end of cupellation with gold beads than with those of silver. The most exact results were obtained when feather litharge was still abundant at the time of brightening.

Furthermore, it is altogether unnecessary to leave gold beads in the muffle for some time after brightening in order to remove the last of the lead, for there is no loss in weight from so doing, but if anything a very slight tendency to increase.

Our results on absorption as influenced by the amount of lead used in cupellation are inconclusive.

The error caused by retention of lead in the beads is one of some magnitude if the results of two careful tests are to be depended on, which showed 0.30 and 0.37 per cent respectively of lead. The amount of this retention is not lessened by leaving the beads in the muffle for some time after brightening.

Silver can be completely extracted from quartation alloys by nitric acid, but more than two repetitions of the acid treatment and subsequent washing are called for if any certainty of complete extraction is to be expected.

Tests made with mixtures of pure nitrous and nitric acids show that the solvent action of the former acid is so slight, if indeed there is any at all, that it need not be considered as a possible disturbing factor in parting.

Similarly, it was shown that the losses in parting with pure nitric acid, whether traces of gold really dissolve or not, are quite negligible, in an ore assay at least.

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

By ARTHUR A. NOYES.

INTRODUCTION.

THE aim of this investigation has been to work out in detail a systematic, universally applicable scheme of qualitative analysis which shall include as nearly as practicable all the metallic elements, and which shall make possible their detection even when present in quantity as small as 1 or 2 milligrams.

The great importance, both from a technological and a purely scientific standpoint, which has become attached in recent years to many of the "rare elements"—so-called often only by reason of their traditional and somewhat arbitrary exclusion from the usual schemes of qualitative analysis—has made it highly desirable that a systematic and reliable method for their detection be available. Any chemist who, without previous experience in this field, has occasion to test for small quantities of these elements will infer upon consulting the existing literature, and become

* It is quite conceivable that some ores, differing from ours in the character of their gangue, may give slags that have greater solvent action on gold.

* From the *Technology Quarterly*, xvi., No. 2.

convinced when he begins to experiment, that his problem is beset with difficulties, and will require much time for its solution.

Until within a few years, aside from the brief outlines given in the text-books on qualitative analysis of Rose, Fresenius, Classen, and a few other writers, nothing like a systematic scheme of analysis existed; and it was necessary for the analyst to apply as best he could the isolated separations and tests recorded in such text-books and in the journals. In 1898, Carnot published in his "*Traité d'Analyse des Substances Minérales*" a scheme of qualitative analysis which included all the more important rare metals. But none of these methods seem to have been subjected to any adequate investigation with reference to the effectiveness of the separations or the reliability and delicacy of the tests; moreover, in a field of work where the closest adherence to the proper conditions is essential to success, the directions given are of a most general character. These schemes, therefore, when tested in the laboratory, are found to be seriously defective, and to have little practical value, except for the detection of large quantities of some of the rare elements. A vast amount of valuable work has, of course been published upon the separation of the rare elements of separate groups, like the rare earths, the platinum metals, and the rarer alkali metals; but this work has been done mainly from the standpoint of quantitative analysis and with reference to the limited number of elements which are found associated in certain important minerals or ores. Of the systematic procedures devised for qualitative purposes ought to be mentioned, however, those of Mylius and Dietz (*Ber.*, 1898, xxxi., 3191), and of Leidie and Quennessen (*Bull. Soc. Chim.*, 1902, [3], xxvii., 181) on the platinum metals, and of Possetto (*Chem. Centralb.*, 1898, i., 634) on the rare earths. These quantitative and qualitative investigations have furnished many of the data necessary for the working out of a complete system of qualitative analysis, such as that which forms the object of this investigation.

This work has been in progress for over three years, and has been carried on in large part by research assistants and advanced students, whose valuable aid will be given recognition in connection with the separate groups of metals upon which each worked. The investigation has been liberally assisted by grants from the Warren Fund of the American Academy of Arts and Sciences, and will be published in its final form in the *Proceedings* of that Academy. It has been thought advisable, however, to make in this journal a preliminary publication of the work, as fast as integral portions of it are brought into satisfactory shape, so that the method may be available at once to those who may desire to use it. The work upon it will be continued, in order to test it more thoroughly and to improve it in matters of detail; but it is not likely that the procedure will be radically modified.

The results will be presented in the form that seems best adapted to the purposes of the analyst. The System of Analysis will be primarily divided into a series of Parts, in each of which will be described, as a rule, the detection of the elements precipitated or otherwise separated by a group reagent. Part I. will treat of the Preparation of the Solution; Part II., of the Analysis of the Tungsten and Niobium Groups; Part III., of the Analysis of the Selenium and Silver Groups; Part IV., of the Analysis of the Platinum Group and the Detection of Lead and Tellurium; Part V., of the Analysis of the Ruthenium, Iridium, Copper, and Molybdenum Groups; and the succeeding Parts, of the Rare Earth, Aluminum and Iron, Alkaline Earth, and Alkali Groups. Under each Part is first presented a Tabular Outline which will give a survey of the important steps and the chemical reactions involved in the procedure. This is followed by a General Discussion, in which are presented the reasons for the adoption of the process employed. Then comes the Procedure itself, and the explanatory Notes upon it. Next are presented Confirmatory Experiments and References, which serve to

substantiate the statements made in the Notes, and to justify the details of the Procedure. Finally, are given the Test Analyses, which were made with known mixtures according to the procedure, in order to test its efficiency.

The reader who wishes to get only a general idea of the method and its efficiency will find that the chapters entitled "Tabular Outline," "General Discussion," and "Test Analyses," will suffice for his purpose. The actual analyst will utilise especially those entitled "Tabular Outline" and "Procedure and Notes." Only to investigators in similar lines, or to those who seek the justification of the statements made in the Notes will the chapters on "Confirmatory Experiments and References" be of interest.

The operations are described in the Procedures in much detail; and the reasons for them, the theoretical principles involved, and other incidental matters are presented very fully in the Notes. It may well seem to experienced analysts that the writer has gone to an extreme in this respect; but, in the first place, attention to not obvious details is really essential in many cases in order to secure delicacy of the tests; and, secondly, it has seemed best to make the scheme as effective as possible in the hands of chemists with little experience in this kind of work, even though it involves in some cases rather lengthy descriptions. Even with such a full description, a knowledge of the manipulation of exact qualitative analysis is essential, in order to enable one to detect small quantities of some of the elements. Before analysing an unknown substance, any one using the method for the first time should apply the procedure of each group to a known mixture containing 2 or 3 milligrams of each element.

The directions are almost always given in the form applicable to the case where all elements that could be present are present, the modifications admissible when certain operations lead to negative results being usually sufficiently evident. The scheme is divided into a number of separate "Procedures," a new one being begun whenever the substance has been resolved into two parts (such as a precipitate and filtrate) which are to be submitted to different operations, or whenever two or more collateral procedures converge to a single one. In order to make it possible to see at once the proper sequence of the procedures in an actual analysis, they are numbered consecutively in the description (except that some numbers are omitted at the end of each part to facilitate subsequent revision); and at the beginning of each procedure the one by which the substance was last treated, and at the end of each procedure those by which the two separated portions of it are next to be treated, are referred to by number.

Most of the experiments described under "Confirmatory Experiments and References" are undoubtedly merely confirmations of previously known chemical facts. The application of these facts to the specific conditions of the procedures it was, however, constantly necessary to test; and it has seemed worth while to make the results a matter of record. The experiments are preceded by a reference to the procedure and note to which they relate.

Of the abbreviations employed, only a few need be explained:—G. D. is used for General Discussion; P., for Procedure; N. for Note; C. E. for Confirmatory Experiments; T. A., for Test Analyses. A number within parentheses expresses the specific gravity at 15°; even with diluted acids, the concentration is for brevity usually indicated in this way; thus, HCl (1.02) means an acid made by mixing one volume of HCl (1.12) with five volumes of water. When it is directed to add a variable quantity of a reagent (for example, 5—15 c.c.), the amount used should be adjusted to the size of the precipitate or residue. Certain brief expressions commonly employed in the procedures are fully explained, especially with reference to the manipulative details, under one of the first procedures where they occur; for example, see P. 3, N. 2, as to the exact significance of "evaporate just to dryness," P. 5, N. 6, as to that of "wash the precipitate."

CONDENSATION COMPOUNDS OF CAMPHOR-
OXALIC ACID AND AMINES.*SEVENTH COMMUNICATION ON CAMPHOROXALIC
DERIVATIVES.By J. BISHOP TINGLE, Ph.D., F.C.S.,
and
WILLIAM EDWIN HOFFMAN, Jun., Ph.D.

(Concluded from p. 123).

AMINE DERIVATIVES OF CAMPHOROXALIC ACID (*continued*).

III. Benzylamine.

1. Camphoroxalic acid (5 grms. = 1 molecule) and benzylamine (4.6 grms. = 2 molecules) were mixed in hot alcoholic solution, and, after evaporating off part of the solvent on the water-bath and cooling, a colourless crystalline mass was gradually deposited. After re-crystallisation from alcohol it was obtained in the form of distorted rhombohedra, melting at 147.5° with the evolution of a gas. With alcoholic ferric chloride no colour was produced. Analysis showed it to be benzylamine benzylcamphoformeneaminecarboxylate.

0.2252 grm. substance gave 15.7 c.c. N at 18° and 770 m.m.

Calculated for $C_8H_{14} \begin{cases} C : CCOONH_3CH_2C_6H_5 \\ CO | NHCH_2C_6H_5 \end{cases}$ N. 7.95
Found 8.16

2. When the above compound is heated with sodium hydroxide solution it dissolves, forming sodium benzylcamphoformeneaminecarboxylate. The addition of dilute hydrochloric acid in excess to this solution produces a gummy precipitate, which solidifies after standing in contact with water, and, on re-crystallisation from ethyl acetate forms colourless crystals melting at 140°. In sodium carbonate solution it dissolves with the evolution of carbonic anhydride, and with alcoholic ferric chloride produces no colour. Analysis proves it to be benzylcamphoformeneaminecarboxylic acid.

0.2035 grm. substance gave 0.5396 grm. CO₂ and 0.1395 grm. H₂O.

Calculated for $C_8H_{14} \begin{cases} C : CCOOH \\ CO | NHCH_2C_6H_5 \end{cases}$ C. 72.52 H. 7.35
Found 72.35 7.6

3. Heated above its melting-point, benzylamine benzylcamphoformeneaminecarboxylate gives off a gas which proved to be carbonic anhydride by the production of barium carbonate when it was passed into a solution of barium hydroxide. The fused material, after the evolution of gas had ceased, was re-crystallised from ethyl acetate, and is deposited in colourless prisms melting at 96.5°. With alcoholic ferric chloride no colour is produced. Analysis showed it to be benzylcamphoformeneamine.

0.1885 grm. substance gave 9.8 c.c. N at 16° and 762 m.m.

Calculated for $C_8H_{14} \begin{cases} C : CH \\ CO | NHCH_2C_6H_5 \end{cases}$ N. 6.07
Found 5.45

If benzylcamphoformeneaminecarboxylic acid is heated above its melting-point, it gives off carbonic anhydride and forms a compound melting at 96.5°, identical with that formed by heating the benzylamine salt of the acid.

IV. α -Naphthylamine.

1. Camphoroxalic acid (5 grms. = 1 molecule) and α -naphthylamine (6.4 grms. = 2 molecules) were mixed in

PART I.—PREPARATION OF THE SOLUTION (INCLUDING THE DETECTION OF OSMIUM, SILVER, AND LEAD).
Tabular Outline.

Non-metallic Substance.—Heat 1 grm. with HNO ₃ (1.20), dilute and filter. (P. 1).		Metallic Substance.—Heat 0.5 grm. with HNO ₃ (1.20), evaporate, and heat at 120°. (P. 4).	
Residue.—Heat with HF, evaporate with HNO ₃ , and add HNO ₃ (1.05); (if insoluble fluorides remain, digest with SiO ₂); evaporate, and heat at 120°. (P. 3).		Dehydrated Residue.—Heat with HNO ₃ (1.20), dilute, and filter. (P. 5).	
Solution.—All elements except Si, Nb, Ta, W, Sn, Os, and most of the Sb and Ti. (P. 51).		Residue.—Heat with HF, dilute, and filter. (P. 6).	
Solution.—Niobium and tungsten groups (Nb, Ta, Ti, W, Sn, Sb); sometimes also P, As, Bi, Se, Te, V, Mo, Ge. (P. 31).		Residue (MnO ₂ , PbO ₂ , HgS, Au, and the substances named below under "Residues").—Boil with HCl (1.20), then with aqua regia, dilute, and filter. (P. 7).	
Solution.—Evaporate, add HCl (1.02), filter. (P. 17).		Residue.—Add HCl and filter. (P. 10).	
Solution.—Chlorides of Pb, Mn, Hg, Au, Pt. (P. 71).		Residue.—Fuse with K ₂ S ₂ O ₇ . (P. 12).	
Residue. AgCl, PbCl ₂ , PbSO ₄ , BaSO ₄ , SrSO ₄ . (P. 18).		Distillate. OsO ₄ . (P. 14).	
Light Coloured Non-metallic Residue (BaSO ₄ , some silicates, Al ₂ O ₃ , TiO ₂ , ZrSiO ₄ , SnO ₂ , ThF ₄ , monazite).—Fuse with Na ₂ CO ₃ ; heat with water, and filter. (P. 9).		Residual Solution. (P. 15).	
Dark Coloured or Metallic Residue (C, SiC, MoS ₂ , FeCr ₂ O ₄ , Fe ₂ (CN) ₁₈ , Pt, Ir, Os, Rh, Ru, FeSi ₃ , FeCr ₂ , &c).—Fuse with Na ₂ O ₂ , add water and HCl, and distil into NaOH. (P. 13).			

(To be continued).

* From the American Chemical Journal, xxxiv., No. 3.

alcoholic solution. On evaporating the solvent, greenish yellow crystals were found, which, after purification from alcohol, melt at 165°, with the evolution of gas. With ferric chloride in alcoholic solution no colour is produced. Analysis proved it to be *a-naphthylamine a-naphthylcamphoformeneaminecarboxylate*.

0.1532 grm. substance gave 7.5 c.c. N at 16° and 766 m.m.

Calculated for $C_8H_{14} \begin{matrix} C : CCOONH_3C_{10}H_7 \\ | \\ CO NHC_{10}H_7 \end{matrix}$.. 5.66
 Found 5.75

2. The above salt dissolves when treated with sodium hydroxide solution, forming *sodium a-naphthylcamphoformeneaminecarboxylate*, which, on acidification with dilute hydrochloric acid, forms a yellow precipitate; this, after crystallisation from benzene, melts at 170°, and is found to be identical with the same compound prepared in another way by Bishop Tingle. It dissolves in sodium carbonate with the evolution of carbonic anhydride, and with alcoholic ferric chloride produces no colour.

3. When either of the above *a-naphthylamine* compounds was heated in order to obtain a camphoformeneamine derivative, a gummy substance was obtained, which could not be induced to crystallise from any solvent.

V. Metatoluidine.

1. Camphoroxalic acid (5 grms. = 1 molecule) and metatoluidine (4.8 grms. = 2 molecules) were allowed to react in alcoholic solution. After evaporation, there were deposited fine needles of a pale lemon colour, which, when re-crystallised from alcohol, melted at 126°; with alcoholic ferric chloride no colour was produced. Analysis showed this substance to be *metatoluidine metatolylcamphoformeneaminecarboxylate*.

0.3153 grm. substance gave 19 c.c. N at 25° and 765 m.m.

Calculated for $C_8H_{14} \begin{matrix} C : CCOONH_3C_6H_4CH_3 \\ | \\ CO NHC_6H_4CH_3 \end{matrix}$.. 6.66
 Found 6.78

2. The above salt, when treated with a solution of sodium hydroxide, dissolves, forming *sodium metatolylcamphoformeneaminecarboxylate*, which, on acidification with dilute hydrochloric acid, gives a yellow precipitate. After purification from benzene, crystals are deposited melting at 154°. They dissolve in sodium carbonate solution with the evolution of carbonic anhydride, and with alcoholic ferric chloride give no colour. Analysis shows it to be *metatolylcamphoformeneaminecarboxylic acid*.

0.1497 grm. substance gave 5.65 c.c. N at 10° and 770 m.m.

Calculated for $C_8H_{14} \begin{matrix} C : CCOOH \\ | \\ CO NHC_6H_4CH_3 \end{matrix}$.. 4.47
 Found 4.58

3. Both metatolylcamphoformeneaminecarboxylic acid and its metatoluidine salt on heating gave a gum which could not be obtained pure enough for analysis.

VI. Diethylamine.

1. Camphoroxalic acid (5 grms. = 1 molecule) was allowed to react with an alcoholic solution (3.4 grms. = 2 molecules) of diethylamine. A compound crystallising in colourless needles was obtained, which, when purified by re-crystallisation from alcohol, melts at 139.5° with the evolution of a gas. With alcoholic ferric chloride it gives no colour reaction. By analysis the compound is shown to be *diethylamine diethylcamphoformolaminecarboxylate*.

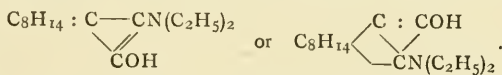
0.1983 grm. substance gives 13.4 c.c. N at 21° and 769 m.m.

Calculated for $C_8H_{14} \begin{matrix} CH.COHC(OONH_2(C_2H_5)_2) \\ | \\ CO N(C_2H_5)_2 \end{matrix}$.. 7.55
 Found 7.80

The diethylamine solution used in the preparation of this compound was prepared by dissolving diethylamine hydrochloride in absolute alcohol, adding the required amount of potassium hydroxide, and filtering off the insoluble potassium chloride.

2. When treated with sodium hydroxide solution, the carboxylate just described dissolves, but, on acidification with dilute hydrochloric acid, it is decomposed into camphoroxalic acid and diethylamine. No method of treatment could be devised by which free diethylcamphoformolaminecarboxylic acid could be obtained.

3. When diethylamine diethylcamphoformolaminecarboxylate is heated above its melting-point, diethylamine, water, and carbonic anhydride are given off, and, after purification of the fused material by crystallisation from acetone, the product melts at 153°. With alcoholic ferric chloride the reddish violet colour is produced which is so characteristic of the enol grouping. By analysis it is found to have an empirical formula identical with that of diethylcamphoformeneamine, but, on account of its behaviour towards ferric chloride, its constitution seems, as previously explained (p. 87), to be represented by the formula—



Analysis.—0.2045 grm. substance gave 8.1 c.c. N at 16° and 762 m.m.

Calculated for $C_{15}H_{25}ON$.. 4.56
 Found 4.68

VII. Dimethylamine.

1. Camphoroxalic acid (5 grms. = 1 molecule) and dimethylamine (2 grms. = 2 molecules) were allowed to react in alcoholic solution, and, after part of the solvent had evaporated spontaneously, a crystalline compound was obtained. After re-crystallisation from acetone, colourless needles were deposited, melting at 137.5° with the evolution of a gas. With alcoholic ferric chloride it produced no colour reaction. Analysis showed it to be *dimethylamine dimethylcamphoformolaminecarboxylate*.

Analysis.

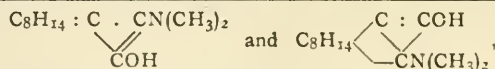
I. 0.2000 grm. substance gave 0.4452 grm. CO₂ and 0.1661 grm. H₂O.

II. 0.2135 grm. substance gave 0.4818 grm. CO₂ and 0.1770 grm. H₂O.

Calculated for—
 $C_8H_{14} \begin{matrix} CH.COHC(OONH_2(CH_3)_2) \\ | \\ CO N(CH_3)_2 \end{matrix}$.. 61.14 9.55
 Found { I. 60.71 9.29
 II. 61.58 9.27

2. When dimethylamine dimethylcamphoformolaminecarboxylate is treated with sodium hydroxide solution it dissolves, but on acidification with dilute hydrochloric acid decomposes into camphoroxalic acid and dimethylamine.

3. When heated to 140°, dimethylamine dimethylcamphoformolaminecarboxylate gives off water, carbonic anhydride, and dimethylamine, and forms a compound which, when purified by re-crystallisation from acetone, melts at 63°. With alcoholic ferric chloride it gives a purple colour. The alternative formulæ,—



for this compound are discussed on p. 88.

Analysis.—0.2458 grm. substance gave 14.8 c.c. N at 19° and 770 m.m.

Calculated for $\text{C}_{13}\text{H}_{21}\text{ON}$	N.
Found	6.77
Found	7.01

VIII. Methylamine.

1. Camphoroxalic acid (5 grms. = 1 molecule) and methylamine (2.8 grms. = 2 molecules) were mixed in alcoholic solution. After evaporation of part of the solvent, colourless needles were deposited; they were purified by re-crystallisation from alcohol and melted at 172°. With alcoholic ferric chloride no colour reaction was produced. Analysis proved the compound to be *methylamine methylcamphorformeneaminecarboxylate*.

Analysis.—0.2147 grm. substance gave 20 c.c. N at 14° and 766 m.m.

Calculated for $\text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{C} : \text{CCOONH}_3\text{CH}_3 \\ \diagdown \text{CO NHCH}_3 \end{array}$	N.
Found	10.51
Found	11.04

2. When treated with sodium hydroxide, the above salt dissolves, but on acidification with dilute hydrochloric acid decomposes into camphoroxalic acid and methylamine.

3. Upon heating at 175°, methylamine methylcamphorformeneaminecarboxylate gives off methylamine and carbonic anhydride, and forms a compound which, when re-crystallised from ethyl acetate, melts at 131°. With alcoholic ferric chloride, no colour reaction is produced. Analysis proved it to be *methylcamphorformeneamine*.

Analysis.—0.2131 grm. substance gave 13.3 c.c. N. at 11° and 766 m.m.

Calculated for $\text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{C} : \text{CH} \\ \diagdown \text{CO NHCH}_3 \end{array}$	N.
Found	7.25
Found	7.50

IX. Benzamidine.

Free benzamidine (2.2 grms. = 1 molecule) was obtained by dissolving the hydrochloride in absolute alcohol, adding the required amount of potassium hydroxide, and filtering off the insoluble potassium chloride. When camphoroxalic acid (5 grms. = 1 molecule) is allowed to react with such an alcoholic solution of benzamidine and the solvent is permitted to evaporate spontaneously, a compound is obtained which may be purified by re-crystallisation from alcohol. It is deposited in colourless prisms; these melt at 184°, evolve a gas, char, and decompose. With alcoholic ferric chloride no colour reaction is produced, and neither acid nor alkali seem to cause any change in the composition of the compound. When heated above its melting-point, it decomposes completely to a carbonaceous mass, from which it is impossible to obtain any definite compound. It did not dissolve in sodium carbonate solution. Analysis proved it to have the empirical formula $\text{C}_{19}\text{H}_{24}\text{O}_4\text{N}_2$. Its probable constitution is discussed on p. 88.

0.1539 grm. substance gave 0.3723 grm. CO_2 and 0.0963 grm. H_2O .

0.2147 grm. substance gave 15.5 c.c. N at 19° and 766 m.m.

	C.	H.	N.
Calculated for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_4$..	66.27	6.97	8.14
Found	65.93	7.002	8.30

X. Benzidine.

Camphoroxalic acid (5 grms. = 1 molecule) and benzidine (4 grms. = 1 molecule) were mixed in hot alcoholic solution. When cooled, this deposited a dense mass of

greenish yellow microscopic needles, which, on account of its very sparing solubility in all the ordinary organic media, was extracted with ether to remove any camphoroxalic acid and benzidine. The residue after this treatment formed a fine powder, which gave no colour reaction with alcoholic ferric chloride, and was not affected by acids or alkalis. It melts at 190°, and when heated above this temperature it decomposed to a carbonaceous mass. It is insoluble in sodium carbonate. Analysis proved it to have the empirical formula $\text{C}_{24}\text{H}_{26}\text{O}_3\text{N}_2$; its possible constitution is discussed on p. 88.

0.1489 grm. substance gave 9.4 c.c. N at 21° and 775 m.m.

Calculated for $\text{C}_{24}\text{H}_{26}\text{O}_3\text{N}_2$	N.
Found	7.18
Found	7.31

XI. Parvanitroorthotoluidine.

When camphoroxalic acid (5 grms. = 1 molecule) and nitrotoiluidine (6.8 grms. = 2 molecules) are heated at 150° under pressure in alcoholic solution for four hours, a yellow compound is obtained which is purified by re-crystallisation from alcohol. It is deposited in bright yellow needles melting at 192°. This compound is unaffected by acids or alkalis, does not dissolve in sodium carbonate, and produces no colour reaction with ferric chloride in alcoholic solution. Considerable difficulty was experienced in the combustion of the substance for the determination of nitrogen; even when the heating was done most cautiously, explosions occurred, so that the analytical results were unreliable. These explosions were probably due to the presence of the nitro group in the compound. The difficulty was overcome in a thoroughly satisfactory manner by mixing the substance with aluminium powder; under these conditions the nitrogen was evolved during the combustion in a stream which could be easily regulated.

Analysis.—0.2145 grm. substance gave 8.8 c.c. N at 17° and 765 m.m.

Calculated for $\text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{C} : \text{CH} \\ \diagdown \text{CO NHC}_6\text{H}_3(\text{CH}_3)\text{NO}_2 \end{array}$	N.
Found	4.66
Found	4.79

XII. Semicarbazine.

Semicarbazine hydrochloride (5 grms. = 2 molecules) was dissolved in as little cold water as possible, and added to an alcoholic solution of potassium acetate (5 grms. = 2 molecules); this solution was then mixed with an alcoholic solution of camphoroxalic acid (5 grms. = 1 molecule). After evaporation of most of the alcohol on the water-bath the solution was greatly diluted with water; a white crystalline precipitate was produced which, on purification by re-crystallisation from alcohol, formed colourless prisms melting at 200°. When dissolved in boiling glacial acetic acid and precipitated by the addition of alcohol, clusters of colourless microscopic needles are deposited; these melt at 209–210°, and correspond to the compound described by Bishop Tingle (*Journ. Am. Chem. Soc.*, 1901, xxiii., 373) as one of two substances formed by the action of semicarbazine on potassium camphoroxalate in alcoholic solution at 100° under pressure. The presence of a second compound, stated by him to be deposited from acetone in colourless needles melting at 218° was not observed; it is apparently not formed under the conditions employed by us. When the compound melting at 209–210°, obtained from acetic acid solution, was dissolved in sodium carbonate solution and precipitated by acids, it formed a jelly, which, after having been dried and re-crystallised from acetic acid, had the same melting-point as before, viz., 209–210°. If the original compound from alcohol, melting at 200°, is re-crystallised from acetone, its melting-point remains constant. With alcoholic ferric chloride, neither substance produces a colour reaction. Both dissolve readily in sodium carbonate, and, as has been stated,

are precipitated by acids from this solution as colourless jellies. Analysis showed that both compounds have the composition of *semicarbazinecamphoformeneaminecarboxylic acid*.

0.2145 grm. substance gave 0.4373 grm. CO₂ and 0.1261 grm. H₂O.

	C.	H.
Calculated for $C_8H_{14} \begin{matrix} C : CCOOH \\ \\ CO \end{matrix} NHNHCONH_2$	55.6	6.76
Found	55.5	6.57

The possible constitution and relationship of these compounds has been discussed on p. 102.

XIII. Orthophenylenediamine.

Camphoroxalic acid (5 grms. = 1 molecule) and orthophenylenediamine (2.4 grms. = 1 molecule) were allowed to react in alcoholic solution. The evaporation of the solvent yielded a deposit of fine yellow needles, which melt at 246°. This substance is identical with the compound obtained by J. Bishop Tingle (*Journ. Am. Chem. Soc.*, 1901, xxiii., 375). The proportional quantities of the reacting materials and the conditions of the experiment were varied, but in all cases the same compound was obtained.

The action of camphoroxalic acid on acetylphenylhydrazine, carbamide, paranitraniline, paramineacetophenone, methylaniline, ethylaniline, benzylaniline, ethylenediamine, benzylphenylhydrazine, quinoline, pyridine, dimethylaniline, orthotoluidine, parabromphenylhydrazine, and hydrazine was tried under conditions similar to those already described for other amines, but in no case could a definite compound be obtained. The reaction products were usually gummy substances which could not be obtained in a crystalline form. They were heated for some time at 150–180° in the hope of forming compounds of the camphoformeneamine type, but from these products also no crystalline derivatives could be isolated by the use of the ordinary organic solvents.

Possibly further investigation of the compounds may result in their purification by distillation under very low pressures.

ACTION OF ACYLATING AGENTS ON CAMPHOFORMENEAMINE DERIVATIVES.

Paratolylcamphoformeneamine (3 grms. = 1 molecule) and acetyl chloride (2.6 grms. = 3 molecules) were boiled in solution of anhydrous ether for about six hours; the ether was then evaporated, leaving a compound which crystallised from alcohol in colourless needles melting at 161°. Analysis showed it to be *acetyl paratolylcamphoformeneamine*.

0.1056 grm. substance gave 0.2992 grm. CO₂ and 0.0705 grm. H₂O.
0.5403 grm. substance gave 0.0983 grm. Mg₂P₂O₇ = 0.0747 grm. C₂H₃O.

	C.	H.	CH ₃ CO.
Calculated for— $C_8H_{14} \begin{matrix} C : CH \\ \\ CO \end{matrix} N \begin{matrix} C_6H_4CH_3 \\ \\ COCH_3 \end{matrix}$	77.4	7.74	13.78
Found	77.26	7.47	13.82

Phenylcamphoformeneamine was treated with phenylsulphonic chloride by the Schotten-Baumann method; 1 grm. (= 1 molecule) of phenylcamphoformeneamine was shaken with 1 grm. (= 7 moles) of sodium hydroxide in 10 per cent aqueous solution, and 3.5 grms. (= 5 molecules) of phenylsulphonic chloride, which were added alternately and in small quantities; a compound is finally obtained which by crystallisation from benzene is deposited in stout colourless needles melting at 133°. Analysis shows it to be *phenylcamphoformeneaminephenylsulphone*.

0.2246 grm. substance gave 0.1311 grm. BaSO₄.

	S.
Calculated for $C_8H_{14} \begin{matrix} C : CH \\ \\ CO \end{matrix} N \begin{matrix} C_6H_5 \\ \\ O_2SC_6H_5 \end{matrix}$	8.10
Found	8.07

β-Naphthylcamphoformeneamine (2 grms. = 1 molecule) and chloracetyl chloride (2.1 grms. = 3 molecules), when boiled for some hours, in anhydrous ether, react to form a bright red substance, which was purified by distillation under diminished pressure. It boiled at 116°, under 45 m.m. pressure and condensed to a colourless crystalline solid, which could be further purified by means of petroleum ether. From this it was deposited in colourless needles melting at 63°. The compound dissolved in sodium-hydrogen carbonate, with evolution of carbonic anhydride, and gave no colour reaction with ferric chloride. It is very unstable, and consequently could not be obtained in a state of purity sufficient to give concordant results on analysis.

The work described in the preceding pages will be continued and extended in various directions. The cost of the greater part of the chemicals which we have used in carrying it out has been defrayed by a grant from the Carnegie Institution; for this we desire to express our thanks and obligations.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 9th, 1906.

Dr. C. CHREE, Vice-President, in the Chair.

PROF. H. A. WILSON read a paper on "*The Velocities of the Ions of Alkali Salt Vapours at High Temperatures.*"

This paper contains a summary of previous work on the velocities of the ions of alkali salt vapours in flames and gases at high temperatures. It is shown that all the results so far obtained are consistent with the view that any salt of caesium, rubidium, potassium, sodium, or lithium gives in a Bunsen flame negative ions having a velocity of 1000 c.m. per sec. for one volt per c.m., and positive ions having a velocity of about 80 c.m. per sec. This result can be explained by supposing that each salt molecule emits a negative corpuscle which forms the negative ion, and that the rest of the molecule forms the positive ion.

Mr. D. OWEN asked Dr. Wilson how, in reference to the theory that the positive ion is the salt molecule minus an electron, he accounted for the fact, shown in his experiments, that the velocity of these ions was independent of their mass.

Dr. WILSON remarked that the positive ion probably acted as a centre of condensation, and formed an aggregate of molecules whose size depended only on the positive charge.

Dr. J. A. HARKER read a paper "*On some Experiments on Earth-currents at Kew Observatory.*"

Dr. Harker gave an account of experiments made some years ago at Kew Observatory on the earth-currents produced by electric-traction schemes, and on the disturbances they cause on the self-recording magnetic instruments which are kept continuously running there to register the variations in the declination and the horizontal and vertical forces. For these experiments two large earth-plates were buried in the ground about four feet deep and two hundred yards apart. These were connected through a photographic recording voltmeter of high resistance. On the traces given by this instrument the effect of the trains on the Central London Railway was strikingly shown, and specimen records exhibited clearly indicated the timetable of that railway and also any accidental breakdowns.

The nearest point to Kew, namely, Shepherd's Bush, is about six miles distant. The same disturbances, and also those due to special traction experiments carried out on the system of the London United Electric Tramway Company during the period when the Central London Railway was shut down, were also clearly shown on magnetograph curves. The effects are much greater on the vertical force than on the horizontal force or the declination, the latter being only slightly affected. A second system of investigation was to connect the earth-plates through the primary of a transformer, the secondary terminals of which were connected to a sensitive moving-coil galvanometer of suitable period and damping. Under these conditions the galvanometer recorded a ballistic throw for each movement of a tramway controller, while the slower variations due to magnetic storms and other causes were without effect. A telephone similarly connected gave a perceptible sound for each controller movement.

Dr. CHREE expressed his interest in the paper, and remarked that Dr. Harker had shown how magnetic records were disturbed by earth-currents due to electric-traction schemes some years ago. The state of affairs at the present time was very much worse, and the vertical-force records were so disturbed as to be useless. The author's curves showed that there was a quiet time at night, and Dr. Chree suggested this time for the determination of the absolute values of the magnetic elements.

NOTICES OF BOOKS.

Chemistry of the Proteids. By GUSTAV MANN, M.D. (Edin.), B.Sc. (Oxon). London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1906.

THE author of this work had originally intended to prepare a translation of Prof. Otto Cohnheim's "*Chemie der Eiweisskörper*," but finding that it was desirable to extend the scope of the book in some directions, and that the alterations necessarily made in bringing the subject-matter up-to-date were not inconsiderable, he preferred to re-write the book, basing his work upon the second edition of the German, but allowing himself more latitude in some branches, and also not refraining from expressing opinions not always in agreement with those of Prof. Cohnheim. The result has fully justified his decision, and the English work is certainly an advance on the German, not only because of its greater completeness, but also in other respects. It is impossible in a short notice to call attention to all the valuable improvements and alterations which have been made; the subject-matter has been brought as nearly as possible up-to-date; for instance, the synthesis of albumins, as far as known up to September, 1905, is given in full, and Emil Fischer's work on the polypeptides, now being published in the *Berichte der Deutschen Chemischen Gesellschaft* is abstracted up to as recent a date. The biological aspect of chemistry is specially kept before the reader, but the action of ferments has been treated only very shortly—a wise procedure, for a full discussion would have enormously increased the size of the book, and there is no lack of authoritative text-books on the subject.

Conversations on Chemistry. (Part II.). *The Chemistry of the Most Important Elements and Compounds.* By W. OSTWALD, Authorised Translation by STUART K. TURNBULL. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1906.

THE second part of these "first steps in chemistry" deals with the most important elements and compounds, and is necessarily more descriptive and somewhat less heuristic. It is again the teacher who will learn most from the book, and any objection that could be brought against the use of the first part by the pupil is increased in Part II., for it is

quite inevitable that the method of question and answer should prove less satisfactory when the learner has obtained some grasp of the first principles and is a little more advanced. The author shows to the highest degree the power of imparting interest to what many generations of learners have regarded as necessary drudgery; even the least original of teachers should be able with very little difficulty to arrange a lecture and experimental work, based upon each chapter of the book, and there could be no comparison between the value of the lessons thus based, and those of the usual type; they would be far easier for the pupil to assimilate, and would do him much more lasting good. In the theoretical parts the author has introduced some slight innovations; thus, he first discusses the neutralisation of acids and bases, and thence deduces the quantitative stoichiometrical laws, of which the beginner is apt to get somewhat hazy ideas when they are presented in the more usual way, deduced from the law of gaseous volumes. So also in the treatment of electrolysis, the atomic theory, and, in fact, all the theoretical parts, great originality is displayed. No teacher of inorganic chemistry should fail to obtain the book; he will find in it much food for thought, and his pupils will undoubtedly derive great benefit from it indirectly.

Lehrbuch der Gerichtlichen Chemie. ("Text-book of Forensic Chemistry"). Vol. II. By Dr. GEORG BAUMERT, Dr. M. DENNSTEDT, and Dr. F. VOIGTLÄNDER. Braunschweig: Friedrich Vieweg und Sohn. 1906.

THIS second edition of Dr. Baumert's valuable book has been thoroughly revised and brought up-to-date by Prof. Dennstedt and Dr. Voigtländer, who, during their long association with the Chemical State Laboratory in Hamburg, must have had opportunities which are probably almost unique of studying the problems of forensic chemistry. This volume deals with the detection of falsifications of writing, chiefly by photographic methods, and the application of biological processes to the identification of different kinds of blood, &c.; the illustrations from the photographs have been carefully prepared, and are most instructive. Much of the information given in the book is quite new, never having been published before, and as it is written in as untechnical language as possible, it will perhaps be found of use to others besides chemical experts. The appendix, on problems connected with incendiarism, contains much new matter relating to the detection of petroleum, &c.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 8, February 19, 1906.

Ebullition and Distillation of Nickel, Iron, Manganese, Chromium, Molybdenum, Tungsten, and Uranium.—Henri Moissan.—The author finds that the metals of the iron group have very different boiling-points. Manganese is the most volatile of all, and its distillation can be easily effected before that of lime; after this comes nickel, which boils very quietly. Chromium distils regularly under the action of a current of 500 amperes under 110 volts pressure. The ebullition of iron is much more difficult to obtain, and it is preceded by a violent evolution of the gases which this metal dissolves with so much ease. However, by employing more intense currents, and after the first effervescence has calmed down, the ebullition of iron becomes more regular; in twenty minutes, with a current of 1000 amperes under 110 volts pressure, the author distilled 400 grms. of iron. Uranium has a still higher boiling-point; ebullition not being produced until

700 ampères is reached. Molybdenum has not been boiled with a current of 700 amperes. The crystalline powder obtained in all these experiments by condensation of the metallic vapour possesses the same chemical properties as the metal reduced to a fine powder.

Syntheses of Tertiary Alcohols prepared from Paramethylcyclohexane.—Paul Sabatier and A. Mailhe. —Methylcyclohexanone-1.4, which can easily be prepared from paracresol, reacts energetically on organo-magnesium chlorides, bromides, or iodides, such as RMgBr ; and the action of water on the crystalline mass obtained gives tertiary alcohols of the general formula $\text{CH}_3-\text{CH} < \begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ \text{CH}_2-\text{CH}_2 \end{smallmatrix} \text{COH}-\text{R}$.

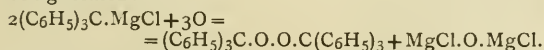
Radio-activity from Springs of Potable Water.—F. Dienert and E. Bouquet.—In order to investigate the natural processes of purification by the soil, and to explain why certain springs emerging from subterranean fissures before filtration do not contain *Bacillus coli communis*, the authors measured the radio-activity of certain springs under the city of Paris.

Condensation of Acetylenic Nitriles with Phenols. General Method of Synthesis of Acrylic β -Oxyphenol- β -substituted Nitriles.—Ch. Moureu and I. Lazennec.—The authors' recent experiments have proved that the acetylenic nitriles, $\text{R}-\text{C}\equiv\text{C}-\text{CN}$, can be condensed with alcohols, giving addition products which result in the fixation of the alcohols on to the acetylenic liaison. It is known that phenols form with the same nitriles analogous addition compounds. This reaction should be comparable to that of the condensation of the phenols and thiophenols with ethyl phenylpropionate and ethyl acetylene dicarbonate, and also to that of the alcohols and phenols with the acetylenic ethers and the acetylenic acetones. In the series of compounds which the authors prepare, a phenolic molecule is fixed on to the acetylenic liaison of the acetylenic nitriles. The hydrolysis of these compounds enables their constitution to be established.

Presence of Formic Aldehyde in Caramelised Substances.—A. Trillat.—The author shows that methylic aldehyde is formed during the incomplete combustion of a number of substances, especially sugar and other substances rich in carbohydrates. He finds that formic aldehyde is found, not only in the gaseous products of these combustions, but also in the residue that is in the caramel, and as a result of a series of experiments finds that sugar at the beginning of caramelisation contains more or less considerable portions of formaldehyde, which influence the original properties. In fact, in sugar refineries it frequently happens that some canes ferment with difficulty, and the formation of methylic aldehyde, owing to the overheating of the cane, offers a very reasonable explanation.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 3, 1906.

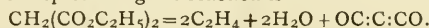
Magnesium Compound of Triphenylchloromethane.—Julius Schmidlin.—When triphenyl iodo-methane is heated for days with magnesium and benzophenone no magnesium compound is formed, nor when triphenylchloromethane in ethereal solution is heated with pure magnesium; but if a small quantity of iodine is added a reaction at once takes place, and the ether compound of magnesium triphenylchloromethane separates out as a yellow crystalline powder. This magnesium compound could not be analysed because it is very readily oxidised by the oxygen of the air, but the composition appears to correspond to the formula $(\text{C}_6\text{H}_5)_3\text{C}.\text{MgCl}$. When oxidised the following reaction takes place, triphenylmethyl peroxide being formed:—



The magnesium compound on addition of water and acids gives a good yield of triphenylchloromethane. By the

action of dry carbon dioxide on the compound triphenyl acetic acid is formed.

Carbon Suboxide (I.).—Otto Diels and Bertram Wolf.—When phosphorus pentoxide acts upon malonic ester, ethylene and a little carbon dioxide are evolved, besides a gas of very piercing odour. The last of these products the authors have succeeded in isolating in the pure state. They found that it is a new oxide of carbon, to which they gave the name carbon suboxide. It is best prepared by using a large excess of phosphorus pentoxide, and allowing the reaction to proceed at 300° ; the products are condensed by means of liquid air, the ethylene being separated by distillation at the temperature of the room. The equation representing the reaction is—



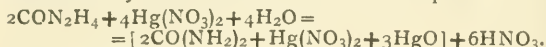
Carbon suboxide is a colourless, refracting, very mobile liquid, possessing a piercing odour, resembling that of acrolein and mustard oil. It attacks the eyes, nose, and respiratory organs, and produces suffocation when breathed in large quantity. It boils at 7° (761 m.m.), but the tension of its vapour is considerable long before the boiling-point is reached. It burns with a smoky blue-edged flame. In all its reactions it behaves like an anhydride of malonic acid. When mixed with water it goes at once into solution, and on evaporating a crystalline mass of malonic acid is left behind. With aniline it yields malonanilide, and it reacts energetically with ammonia, malonamide being formed. With hydrochloric acid it gives malonyl chloride. When it is sealed up in glass tubes and allowed to stand for a day or two at 15° , the liquid slowly turns yellow, and yellow flakes are deposited, which finally form a dark red mass. This mass when rubbed up gives a black powder, the analysis of which gave conflicting results. The preparations thus obtained are soluble in cold water, yielding an intense eosin red colouration. At 37° the decomposition proceeds much more quickly, and at 100° it takes place in a few moments. Elementary analysis showed that the formula of carbon suboxide is C_3O_2 , and when a measured volume was exploded with oxygen the volume of the gases before and after the explosion was the same, as shown by the equation $\text{C}_3\text{O}_2 + 2\text{O}_2 = 3\text{CO}_2$. The vapour density (determined by Hofmann's method) corresponds to the formula C_3O_2 . In composition and properties carbon suboxide recalls the metal carbonyl compounds, especially nickel carbonyl,—



Allotropic Forms of Selenium.—Robert Marc.—The author's experiments, performed with carefully purified selenium, have shown that two very different forms of metallic conducting selenium exist. The grey crystalline form, obtained by heating amorphous selenium, is labile. Denoting this form by A, the author has shown that A goes over into the second form B practically at all temperatures, and with measurable velocity above 170° . This change is accompanied by development of heat. Modification A is a very bad conductor of the electric current at the temperature of the room. On warming, its conductivity rapidly increases, and reaches about twenty times its original value at 170° , and on converting form A into form B the conductivity also increases, being ten times the conductivity of A at 170° ; this increase, however, takes place very slowly. It was to be expected that form B would be the stable form of selenium at all temperatures, but this was not the case. If it was rapidly cooled, the conductivity increased, and at the temperature of the room the conductivity of form B is 1000 to 2000 times greater than that of A. However, when allowed to stand at the temperature of the room the conductivity steadily decreased. It was further found that in the interval 217° to 160° there was equilibrium between the two modifications of selenium, which recalls the analogous case of sulphur for which equilibrium exists between the forms $\text{S}_8 \rightleftharpoons \text{S}_6$ between

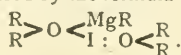
120–448°; the equilibrium occurs in the liquid phase for sulphur and in the solid for selenium. Amorphous selenium appears distinctly red in thin layers, form A is metallic grey with a faint reddish glimmer, and form B is blue-grey. Amorphous selenium is exceedingly brittle, form A less so, but may easily be powdered, while B is ductile. Neither A nor B is soluble in pure carbon disulphide at the temperature of the room, and the conflicting evidence of other workers upon this and other points is to be ascribed to the impurity of their preparations. Pure selenium shows a very great power of attacking metals, e.g., platinum, and differs in many ways from the impure element.

Quantitative Determination of Urea.—B. Glassmann.—The principle of the method is a modification of Liebig and Pfluger's. First of all, phosphoric acid and sulphuric acid are removed by precipitation with barium nitrate and baryta water; the filtrate is precipitated with nitric acid and silver nitrate, and to the liquid a known excess of titrated mercuric nitrate solution is added, neutralising with sodium carbonate. The precipitate is filtered off, the filtrate acidified with nitric acid, and cold iron alum solution and 30 per cent nitric acid are added till all colouration is removed. The liquid is then titrated with rhodan-ammonium in the usual way till the light brown colour is permanent. Thus the excess of mercury is obtained, and from this may be calculated the urea. The equation is—



This method gives very accurate results, and it has the advantage that the concentration of the urea solution has no influence on the results, as is the case in Liebig's method.

New Series of Ether Complexes of the Magnesium Organic Compounds.—W. Tschelintzeff.—The author has shown that magnesium iodide under ordinary circumstances and in presence of an excess of ether yields a compound of the formula $\text{MgI}_2 \cdot 4(\text{C}_2\text{H}_5)_2\text{O}$. Both analytical and thermic experiments show that when magnesium organic compounds are prepared by Grignard's method, ether complexes containing not one but two molecules of ether are formed. The structure of these compounds is satisfactorily expressed by the formula—



Some other compounds are known in which the halogens appear to be polyvalent.

MEETINGS FOR THE WEEK.

- MONDAY, 26th.—Society of Arts, 8. (Cantor Lectures). "Fire, Fire Risks, and Fire Extinction," by Vivian B. Lewes.
TUESDAY, 27th.—Royal Institution, 5. (Tyndall Lectures). "The Influence of Geology on Scenery," by John E. Marr, F.R.S., &c.
WEDNESDAY, 28th.—Society of Arts, 8. "Coal Conservation, Power Transmission, and Smoke Prevention," by Arthur J. Martin, M.Inst.C.E.
THURSDAY, 29th.—Royal Institution, 5. "Internal Combustion Engines" (with Experimental Illustrations), by Prof. Bertram Hopkinson, M.A., &c.
FRIDAY, 30th.—Royal Institution, 9. "Recent Progress in Magneto-optics," by Prof. P. Zeeman.
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VOL. XCIII., No. 2418.

ON THE EFFECT OF CALCIUM IN DEVELOPING THE PHOSPHORESCENCE OF SOME RARE EARTHS.

By Sir WILLIAM CROOKES,

Hon. D.Sc. (Oxford, Dublin, and Cape of Good Hope), F.R.S.

On several occasions arguments have been brought against my views on phosphorescence spectra and their value as tests of elementary bodies. It has been ascertained that, while crude yttria may phosphoresce brilliantly and show the citron (or G δ) line with great brilliancy, highly purified yttria either phosphoresces feebly or not at all. It therefore has been argued that, if a 50 per cent yttrium earth gives the citron line well, and a 100 per cent yttrium earth does not show it at all, therefore the body showing the line resides in the 50 per cent of extraneous matter and not in the 50 per cent of yttria.

The effect of lime and similar bodies in bringing out the phosphorescence of yttria was early forced on my notice. Indeed at first (*loc. cit.*, par. 9) I was inclined to believe that the citron band was actually characteristic of calcium pure and simple, and it was not till I remembered the remarkable result produced in the absorption spectrum of some jargons by the presence of a minute trace of uranium (CHEMICAL NEWS, vol. xix., pp. 121, 142, 205, 277; vol. xx., pp. 7, 104; vol. xxi., p. 73) that I tried the effect of traces of other bodies in educing the citron band.

A systematic series of experiments was made in 1883 (*Phil. Trans. Roy. Soc.*, 1883, Part III., p. 916—917) to ascertain the exact effect of different quantities of lime added to yttria in modifying the phosphorescence spectrum, and the proportions were varied between the limits of $Y/Ca = 1/100$ and $Y/Ca = 1/1000000$. The citron band was visible in all these mixtures, and even when there was a million times as much lime as yttria there was no mistaking its presence, and I said I had no doubt a smaller quantity of yttria could be detected.

In a paper "On the Fractionation of Yttria," read before the British Association in 1886 (CHEMICAL NEWS, vol. liv., p. 155), I said:—"By mixing together yttria and lime . . . the phosphorescing energy of the lime does not spend itself over the whole spectrum, but concentrates itself in greatly reinforcing the yttria bands." Again, speaking of the addition of 10 per cent of lime to alumina containing a trace of yttria, I said:—"The calcium brought out the yttrium band" (*Proc. Roy. Soc.*, vol. xlii., p. 29).

In a paper on "Radiant Matter Spectroscopy," read before the Royal Society in 1887 (*Proc. Roy. Soc.*, xlii., p. 115), I gave a long series of experiments undertaken with a view of ascertaining what was the action of lime on the phosphorescing properties of yttria. I said:—"The effect of calcium on the phosphorescence of yttria and samaria has been frequently referred to in my previous papers; it may save time if I summarise the results here. About 1 per cent of lime added to a badly phosphorescing body containing yttrium or samarium always causes it to phosphoresce well; it diminishes the sharpness of the citron line of G δ , but increases its brightness; it also renders the deep blue line at G α extremely bright. The green lines of G β are diminished in brightness. Lime also brings out the phosphorescence of samarium, although by itself—or in the presence of a small quantity of yttrium—samarium scarcely phosphoresces at all."

The following extract from my paper on the element samarium (*Phil. Trans. Roy. Soc.*, 1885, Part II., Samarium) illustrates the remarkable effect of lime upon the phosphorescence spectrum:—

"Ultimately two portions of substance were produced—a precipitate (113), containing the supposed new element; and a filtrate, containing the strontium, calcium, and other impurities. Neither the precipitate nor filtrate, tested in the usual manner, showed the orange band anything like so well as the material before such separation, and, indeed, at this stage of the experiments it frequently vanished altogether. Some of the filtrate and precipitate were now mixed together, treated with sulphuric acid, and tested as before; they gave the orange-band spectrum as brightly as did the original substance. The ammonia precipitate might contain any or all of the rare earths. Chemical analysis showed nothing but a calcium salt in the filtrate. Could it be that the union of two bodies was necessary to give this spectrum, and that calcium was one of these?"

"A new factor must now be taken into account—the presence of a calcium compound appears to be necessary. An earthy body which, when treated and tested in the usual manner, fails to show the faintest glow of an orange-band spectrum, can by admixture with calcic sulphate be made to yield a pure and brilliant spectrum."

Besides calcium, many other bodies possess the property of revealing or enhancing the phosphorescence spectrum, and a good many experiments were made upon this point.

"The metals used to mix with it were in the form of sulphates—strontium, barium, glucinum, zirconium, thorium, magnesium, zinc, cadmium, lead, copper, silver, cerium, lanthanum, didymium, aluminium, manganese, tin, bismuth, antimony; also silicic, titanic, tantallic, tungstic, molybdic, and niobic acids. More than half of these bodies possessed the property of conferring 'orange-band' phosphorescence on the precipitate under examination, although by themselves they evinced no power of giving a phosphorescent spectrum."

"Of the great number of bodies used to mix with the earth x (samaria) in these experiments, which acted best?" Ultimately I came to the conclusion that lime, if not the best, was as good as any."

I have also shown that the character of the spectrum produced by a given earth varies very considerably with the particular compound used, the oxides generally giving rise to what I have termed "sharp-line spectra" (*Chem. Soc. Journ.*, Ann. Gen. Meet., March 21, 1889, vol. lv., p. 277); and the sulphates, phosphates, &c., more or less nebulous, shaded bands.

M. Urbain in a communication to the French Academy (*Comptes Rendus*, 1905, vol. cxli., p. 954) suggests that the material giving the group of bands in the ultra-violet spectrum, that I have attributed to an element "victorium," is in reality gadolinium, attempting to overcome the difficulty that this latter earth in its pure state does not show the bands, or at most only shows them very feebly, by suggesting that an "exciting element" is needed to bring out the bands, and the paper in question contains the photograph of a spectrum showing a group of bands very similar in appearance to the victorium group but of slightly different wave-length.

As this difference in the wave-length of a definite group of bands seemed of importance, an attempt was made to get this group together with iron on an instrument of large dispersion; the five-prism quartz spectrograph was used, and an earth very rich in Vc was taken, an exposure of six hours being given; the resulting photograph showed that the main band was double, the centres of its two components being at $\lambda 3116.6$ and $\lambda 3119.5$, the centre of the blank space between them being at $\lambda 3118.0$, and the whole double band extending from wave-length 3115.2 to 3120.7 . The Gd-Ca bands of M. Urbain occur between wave-lengths 3136 and 3155 .

I have made some experiments to show the effect produced by added lime, both in the form of sulphates and oxides. The details of the experiments are as follows:—

Lime added to M. Urbain's pure europia failed to bring out more than the faintest trace of the Vc bands, but gave

a great concentration of light between wave-lengths 4385 and 3613.

The addition of a small quantity of lime to some pure gadolinia recently received from M. Urbain did not produce any important variation in the phosphorescence spectrum, which was but little different from that given by the pure earth. Another mixture containing 80 per cent of lime with 20 per cent of the pure gadolinia, prepared in the manner described by M. Urbain, viz., by precipitating the mixed earths from their solution as carbonates, and converting them into oxides by ignition, gave only a very faint band in Urbain's new position, λ 3136 to λ 3155.

The phosphorescence spectrum given by the above described mixture containing 80 per cent of lime was again photographed, and then without touching the photographic film the mixed oxides were removed from the vacuum tube, converted into sulphates, returned, and the cathodic spectrum again photographed in such a way that the second spectrum came just below the first.

In the resulting photograph the spectrum given by the oxides consists chiefly of a faint band in Urbain's position, λ 3136 to λ 3155, while that given by the ignited sulphates consisted of bands of the same character and wave-lengths as in the Victoria spectrum.

A mixture was now made of an earth known to be rich in victorium, and pure lime, the latter earth being in about the same proportion as before; this mixture was photographed both as oxide and sulphate on the same film in the way already described; the resulting photograph showed change of character and position in the victorium group in the oxide, and also many other less refrangible lines that are not seen in pure gadolinia.

Further more exact experiments were now made. The victorium earth that was last used was very carefully purified from any lime that might have been present, and a quantity was made into a 10 per cent solution as nitrate.

Some clear crystals of calc-spar were taken, and this also was made into a stock solution containing 10 per cent Ca.

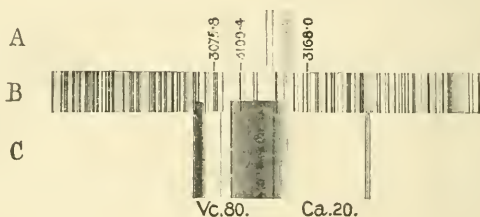
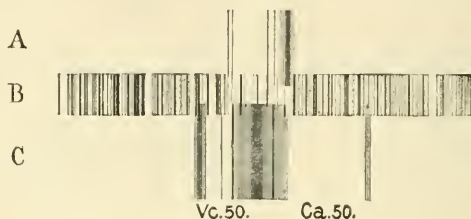
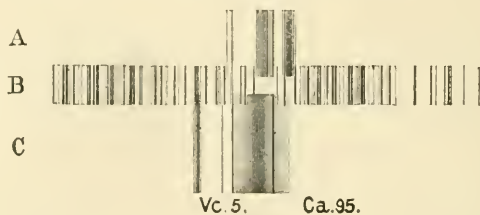
This victorium earth although not pure could have contained little, if any, gadolinium; in the experiments the various proportions of the 10 per cent solutions were mixed together, precipitated by ammonium carbonate, washed, dried, the carbonate calcined at a bright yellow heat, and the cathodic spectrum of the resulting mixed oxides photographed; then, without disturbing the optical arrangements, the oxides were converted into sulphates and their cathodic spectra again photographed, so that the two spectra were one below the other on the same film; the spectrum of iron being interposed as a standard. Three experiments were made with mixtures of Vc + 95 per cent Ca, Vc + 50 per cent Ca, and Vc + 20 per cent Ca. The resulting spectra show that as the proportion of victorium increases, the intensity of the victorium group of bands as given by the sulphates also increases, the mixture of Vc 80 and Ca 20 giving the group in its old character and with considerable intensity; but the most remarkable feature in these compound spectra is that the oxide group of Vc bands is strongest in the mixture containing the smallest proportion of victorium, and they fade out as the proportion of victorium increases, exactly the reverse to the behaviour of the sulphates.

Calcium oxide alone was next tried, and in this case there was a complete absence of the Vc bands, the spectrum giving only a concentration of light in the less refrangible part and a nebulous band in the yellow-green.

Converting this oxide into sulphate changed the cathodic luminescence from golden yellow to bright green, and the photographed spectrum shows a concentration of light in that position.

The victorium earth that has been used in the experiments just described, although rich in Vc, is not by any means so pure as has been obtained from time to time, and in none of these can the percentage of gadolinia as an impurity be at all large. This fact in itself is against the probability of Vc being gadolinia + an exciting agent.

I have many photographs of victorium spectra that show the bands with far greater intensity than I have seen them by using any of M. Urbain's gadolinia earths.



A = Ignited oxide.
B = Iron spark.
C = Ignited sulphate.

M. Urbain's suggestion that Vc is Gd + an exciting agent is improbable, because by no treatment or addition of Ca have I been able to get with pure gadolinia so strong a victorium band as with my old fractions. Moreover, as shown above, the VcCa band is different in character and wave-length from the Vc band.

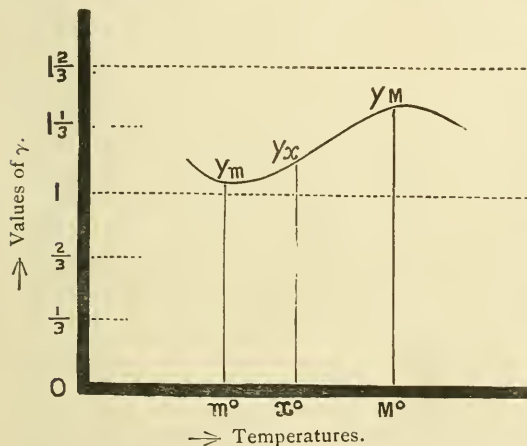
The Chemical Laboratory Fresenius at Wiesbaden. — During the Winter Term, 1905-6, the Chemical Laboratory Fresenius was attended by 47 students. Of these, 35 were from Germany, 4 from England, and 1 each from France, Holland, Hungary, Russia, Spain, Sweden, the United States of America, and Chili. There were three assistants in the Instruction Laboratory and twenty-five in the Versuchsstationen (private laboratories). To the teaching staff of the Institution belong the Directors, Geh. Regierungsrat Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Prof. Dr. med. G. Frank, Dr. L. Grünhut, Dr. R. Fresenius, and Architect J. Huber. The Summer Term begins on April 24th. In the Winter Term, 1905-6, besides scientific work, there were many examinations carried on in the different departments of the Laboratory (Versuchsstationen) in the interests of trade, industry, mining, agriculture, hygiene, justice, and government.

QUANTITATIVE RELATION BETWEEN THE SPECIFIC HEATS OF A GAS AND ITS MOLECULAR CONSTITUTION.

By PHILIP BLACKMAN.

FROM the well-known equation $C_p - C_v = R/J$, we obtain $\gamma = 1 + R/JC_v$, where $\gamma = C_p/C_v$.

So long as the molecular structure of a gas remains unchanged during any range of temperature, the value of R also remains constant for that range of temperature. As C_v increases with increase of temperature, it follows that γ will be a continuously diminishing quantity during that interval of temperature (whether this range is measurably large or infinitely small does not, evidently affect the argument). It is an established experimental fact that, the simpler the molecular structure of a gas (*i.e.*, the fewer the number of atoms constituting the molecule), the greater is this value of γ . Hence, if the molecules of a gas begin to dissociate with increase of temperature, we expect that γ will now become continually increasing, till, finally, when the gas is entirely dissociated into simpler molecules, γ will have attained its maximum value for that molecular condition of the gas. If the molecules beyond



that temperature cease to dissociate until a new temperature is reached, γ will once more reach a minimum value, and then go up again to a new maximum so long as the molecules become still simpler in structure. This process would go on repeatedly until the gas molecules attained their simplest structure (*i.e.*, became monatomic, when γ would reach the greatest of all maxima, *viz.*, $1\frac{2}{3}$).

It now remains to show how γ is related to the percentage molecular decomposition of a gas. Let us examine the curve for γ between a minimum value, γ_m (corresponding to a temperature m°), and the next maximum value, γ_M (corresponding to a temperature M°). At the stage represented by γ_m the gas molecules are all alike in structure, at the stage denoted by γ_M the molecules have all been structurally simplified. Therefore the difference between the ordinates at γ_M and γ_m —*i.e.*, $\gamma_M - \gamma_m$ —is equal to 100 per cent decomposition; and any other value, γ_x (at temperature x°), intermediate between γ_m and γ_M , will evidently correspond, proportionately to a percentage decomposition of $100 \frac{\gamma_x - \gamma_m}{\gamma_M - \gamma_m}$.

A similar formula will be applicable to any range of temperature from one minimum value of γ to the next maximum value.

Thus, by plotting or tabulating the values of γ for any gas, from its critical temperature onwards, the results would furnish a valuable means for studying the variations in the molecular complexity of the gas.

A more correct formula is $100 \frac{l_{\gamma_x - \gamma_m}}{l_{\gamma_M - \gamma_m}}$ (in which $l_{\gamma_x - \gamma_m}$ = length of curve between γ_m and γ_x , and $l_{\gamma_M - \gamma_m}$ = length of curve between γ_m and γ_M).

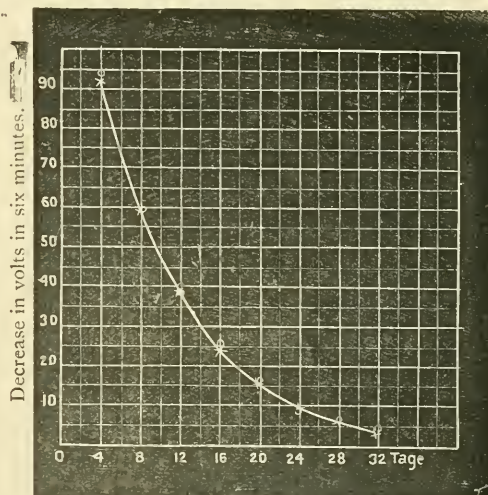
East London Technical College,
London, E.

β-POLONIUM.

By F. GIESEL.

AS is well known, the Curies discovered in a bismuth separation from pitchblende the first radio-active substance, polonium, the rays of which have very little penetrating power, and are thus α -rays.

From the beginning of the Curies' investigations I have frequently prepared polonium from uranium earths of various origin, sometimes in relatively large quantity. My polonium, unlike the Curies', when freshly prepared always gave, besides the α -rays, the penetrating β -rays, so power-



o Observed. × Calculated.

fully that the phosphorescence images could be observed very plainly on the Röntgen screen. I then determined the deviability of these rays by the magnet. The direction of the deviation was the same as I had shown for the β -radium rays. However, I had previously proved a difference in the power of penetration of the β -rays of polonium and radium (*Ann. d. Phys. u. Chem.*, 1899, lxi., 93). The image of the hand, for instance, seems to show stronger contrasts with my polonium rays than with radium rays; the former are more easily absorbed. Probably the γ -rays are altogether absent.

Marckwald then showed how a substance emitting only α -rays could be easily separated from the bismuth salts of pitchblende. He thought that his substance was different from the Curies' polonium, and called it radio-tellurium. But it was shown that, both from my polonium and from the Curies' likewise, Marckwald's substance could be prepared by different methods (*Berichte*, 1903, xxxvi., 728). The Curies' polonium, like mine, contained the substance giving α -rays, but mixed in varying (and vanishing) quantities with bismuth and with an allied substance emitting β -rays.

By immersing bismuth or platinum metals in radium solution, I succeeded in reproducing the radiation phenomena of radio-tellurium (*Berichte*, 1903, xxxvi., 2368),

which seemed to confirm my assumption that polonium is bismuth rendered active by radium induction (according to modern conceptions, a decomposition product of radium). Similarly, Rutherford considers that my induced bismuth, like his radium E obtained from radium emanation, is identical with polonium and radio-tellurium. Finally, M^{de} Curie (*Comptes Rendus*, Jan., 1906, cxlii., 273) has recently found the same constant of decay to the half value—viz., one hundred and forty days—for her polonium as Marckwald found for radio-tellurium, so that there can no longer be any doubt of the identity of the substance which has been prepared in different ways by Curie, Marckwald, and me from the bismuth salts of pitchblende, and which emits only α -rays.

The substance emitting β -rays, which I may call β -polonium for short, has not been investigated by other workers, probably because it decays too rapidly, so that it can only be found in sufficient quantity in rapidly made preparations. As the determination of the decay constants is of importance for the further characterisation of my substance, β -polonium, I took the opportunity of a recent radium extraction to prepare from the raw barium-lead-radium sulphate, by the old method, a bismuth oxychloride which I used for this purpose.

The observations of the decay of the radiation were made in Elster and Geitel's apparatus at intervals of four days; they are collected in the table given below. The intensity of the radiation is put equal to a decrease of the charge in volts within six minutes, using 0.01 grm.

Time, in days.	Intensity of the radiation.		Δ .
	Observed.	Calculated.	
0	—	144.6	—
4	94.0	92.2	+1.8
8	58.4	58.8	-0.4
12	38.2	37.5	+0.7
16	25.4	23.9	+1.5
20	15.6	15.2	+0.4
24	9.4	9.8	-0.4
28	6.6	6.2	+0.4
32	4.2	3.9	+0.3

(Cf. the graphic representation).

In the determination, the α -radiation of the Curies' polonium contained in the preparation could be neglected, because this can arise only in vanishing amounts from the bismuth salts and the paper envelope used. This was shown in one part of the preparation yielding the above curve, from which the part which gave the α -radiation was removed by immersing a strip of copper in the hydrochloric acid solution. The bismuth oxychloride then suffered no appreciable change in the decay of the β -radiation.

The calculation of the intensity of the β -radiation was performed by putting $I = I_0 e^{-at}$.

A comparison experiment showed that if t is measured in days the decay constant has the value 0.1128. The constant of decay to the half value is thence calculated to 6.14, and the mean duration of life of an atom yielding the β -radiation to 8.86 days. As the numbers are not to be found among the time constants of the radium derivatives investigated by Rutherford, further experiments are necessary to explain the eventual position of β -polonium in the series of the decay products of radium.—*Berichte*, 1906, xxxix., 780.

Calcium and Strontium Iodomercurates.—A. Duboin.—The author obtains calcium iodomercurate, $\text{CaI}_2 \cdot \text{HgI}_2 \cdot 8\text{H}_2\text{O}$, in transparent needles, which may attain a length of 5 c.m., by slow evaporation in the air of a liquid of the following composition:—Ca, 3.97 per cent; Hg, 21.84 per cent; I, 52.80 per cent; and water, 21.39 per cent. The density of the crystals is 3.25. He also prepares the corresponding strontium salt, $\text{SrI}_2 \cdot \text{HgI}_2 \cdot 8\text{H}_2\text{O}$.—*Comptes Rendus*, cxlii., No. 10.

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

PART I. (*continued*).—PREPARATION OF THE SOLUTION
(INCLUDING THE DETECTION OF OSMIUM, SILVER,
AND LEAD).

By ARTHUR A. NOYES.

(Continued from p. 136).

General Discussion.

MUCH effort has been devoted to determining the best general method for the preparation of a solution of an unknown substance for the analysis for the metallic elements. That some definite method be adopted for this purpose is an essential preliminary to the working out of a general system of analysis, especially when the rare metals are to be included; for the subsequent division into groups must depend to some extent upon the nature of the acids employed as solvents. The aim has been to devise a method of preparing the solution, which in its actual application to substances ordinarily met with shall be as rapid as possible, which shall be so general and so fully developed as to effect the solution of practically all known substances, and which shall adapt itself to sharp and convenient group-separations in the subsequent system of analysis.

In the usual well-known method of procedure with a non-metallic substance, this is heated successively with water, dilute and concentrated hydrochloric acid, nitric acid, and aqua regia. Then the residue, if blowpipe tests show the absence of much reducible metal, is fused in a platinum crucible with sodium carbonate; or, if reducible metal is present, to remove it the residue is first treated with special solvents like potassium cyanide and ammonium acetate, and is then fused in a platinum crucible; or, if the use of such solvents is inconvenient or ineffective, the residue is fused in a porcelain crucible, whereby the constituents of the crucible are introduced. Finally, any residue undecomposed by the carbonate fusion is fused with such special fluxes, potassium disulphate, sodium carbonate and nitrate, sodium carbonate and sulphur, as the apparent nature of the residue suggests. It will be seen that this procedure is very different from the one summarised in the Tabular Outline given above, which has been adopted as a part of the new System of Analysis. The advantages of the proposed modifications should therefore be presented.

An important consideration having a direct bearing on the procedure to be adopted for the preparation of the solution must be first mentioned. This has reference to the fact that certain oxides, namely, those of silicon, tungsten, niobium, and tantalum, do not dissolve, or at any rate do not remain in solution, in the dilute mineral acids commonly employed; so that, when a substance containing these oxides has been brought into solution by an alkaline fusion or treatment with a special acid like concentrated sulphuric or hydrofluoric acid, they separate upon neutralisation of the alkali or upon dilution or replacement of the acid, either immediately or in some subsequent stage of the analysis. This fact has been ignored in the previous schemes of analysis outlined for the rare elements; thus tungsten, in spite of the insolubility of its oxide in acids, is provided for either in the ammonium sulphide solution of the hydrogen sulphide precipitate, or in the filtrate from the ammonium hydroxide and sulphide precipitate; niobium and tantalum, which are bound to precipitate through hydrolysis of their salts when the solution is diluted and heated in the precipitation with hydrogen sulphide, are commonly included among the elements precipitated by ammonium hydroxide. It is therefore essential, unless these elements are to be allowed to appear somewhat

* From the *Technology Quarterly*, xvi., No. 2.

capriciously at different points in the analysis, to remove them at the start. In order to do this completely, however, it is necessary to evaporate the solution to complete dryness, in order to dehydrate their hydroxides and make them completely insoluble in dilute acid. Even though it is true that certain other elements divide themselves between such a residue and the solution, and must be provided for in the subsequent analysis of both portions, this is a far less serious objection than that justified by the failure to provide for the certain detection of tungsten, niobium, and tantalum. It is for this reason that the first series of operations after the decomposition of the substance with strong acids is directed to effecting the removal of the group of elements whose dehydrated hydroxides are insoluble in dilute acid.

The first solvent employed in the proposed method (P. 1) is nitric acid, not hydrochloric acid; the most cogent reason for this being that, if the latter acid were used, certain elements, namely, arsenic, selenium, germanium, mercury, and gallium, would be wholly or partly lost in the subsequent evaporations, owing to the volatility of their chlorides. Hydrochloric acid also has the disadvantage of causing the precipitation of silver, lead, mercurous and thalious chlorides, and thereby making it impossible to determine whether complete decomposition has been effected. Nitric acid, owing to its oxidising power, is, moreover, a more general solvent; but it does on this very account have the disadvantage of oxidising sulphides to sulphates, and causing the separation of the insoluble sulphates of lead, barium, and strontium; and it is to reduce the amount of this oxidation and to make certain crystalline nitrates, like those of lead and barium, more soluble, that a somewhat diluted acid of the specific gravity 1.20 is recommended. Furthermore, nitric acid, unlike hydrochloric acid, leaves all the tin and almost all of the antimony in the insoluble portion of the dehydrated residue.

The first residue insoluble in nitric acid is not treated at once with aqua regia, because the latter solvent decomposes very few substances unacted upon by the former; because the disadvantages of hydrochloric acid just specified apply to its use in some degree; and because any residue undissolved by it, especially if not thoroughly washed, might retain chlorides which would cause the platinum vessel necessarily used in the next treatment with hydrofluoric acid to be attacked.

The residue undissolved by nitric acid is treated with hydrofluoric acid, for the reason that this forms a simple method of dissolving silica and almost all silicates, which otherwise would have to be decomposed by a fusion with sodium carbonate or some other flux. The fusion with sodium carbonate has the disadvantages that the operation is less convenient; that it introduces alkali metals into the solution, which must therefore be tested for in a separate solution prepared in some other way; and that before the fusion can be carried out in a platinum crucible, the residue must be tested for reducible metals, and, if they are present, freed from them, as far as possible, by treatment with special solvents, like hot concentrated hydrochloric acid or ammonium acetate and potassium cyanide solutions. If, however, it is not desired to test for alkali metals, and if reducible metals are probably absent, the residue insoluble in nitric acid (P. 1) may, if the sodium carbonate fusion is preferred to the treatment here described, be treated at once by P. 7 and then by the subsequent procedures.

Both the free and combined hydrofluoric acid must next be completely removed in order to proceed satisfactorily with the analysis; for, otherwise, partial solution of the oxides of the tungsten and niobium groups would take place, and the glass vessels used in subsequent operations would be attacked. Its removal might be easily accomplished by a single evaporation with sulphuric acid to the point of strong fuming, and this would have the advantage of decomposing a few other substances (such as monazite and thorium fluoride) that are not much attacked by

hydrofluoric and nitric acids. A great many experiments were made to test the applicability of this process of decomposition, so much used in quantitative work, to the purposes of qualitative analysis. It was abandoned, however, because the introduction of sulphuric acid complicates the subsequent procedure by preventing the complete separation of the hydroxides of certain elements of the tungsten and niobium groups when the acid is diluted, and by causing the precipitation of some basic sulphates as well as that of the insoluble neutral ones before it is certain that complete decomposition of the substance has been effected. Its abandonment was, moreover, made possible by the discovery of an alternative method of decomposing the insoluble fluorides. It was found, namely, that all of these except thorium fluoride are destroyed by concentrated nitric acid when its action is supplemented by the addition of finely divided silica. This substance evidently acts by combining with the hydrofluoric acid liberated by the strong nitric acid, thus enabling the reaction to become complete in accordance with the Mass Action Law; it was, in fact, this theoretical consideration that suggested its use.

With by far the larger proportion of substances apt to be submitted to analysis, any portion of the dehydrated residue that may be undissolved by dilute nitric acid (P. 5) consists only of silica and oxides of the tungsten and niobium groups, and dissolves completely when it is treated with hydrofluoric acid (P. 6). Still less frequently will there be a residue after the next treatment with hot strong hydrochloric acid and aqua regia (P. 7); for almost all of the fairly common substances previously unacted upon, such as manganese and lead peroxides, mercuric sulphide, silver chloride, lead strontium, and barium sulphates, gold and platinum, are dissolved by these acids. The lengthy description of subsequent procedures, which is added in order to provide for nearly every possible case, must not therefore give the impression that the method here adopted is in its ordinary application long or complicated.

Of the subsequent fusions necessary in special cases, only that with sodium peroxide (P. 13) need receive any general discussion. This flux, suggested by the work of Leidié and Quenessen (*Bull. Soc. Chim.*, 1902, [3], xxvii., 181) was adopted, because it undoubtedly furnishes the best solution of the difficult problem of bringing the rarer platinum metals into a soluble form. The process usually employed for this purpose consists of two parts:—The metal is first brought into a fine state of division by fusing it with a large quantity of lead and treating the fused mass with nitric acid; the residue is then intimately mixed with sodium chloride, and heated to a dark red heat in a current of chlorine. Both parts of this process are extremely tedious and likely to yield incomplete results, even when only half a grm. of metal is to be treated. On the other hand, when the metal is to be fused with sodium peroxide, mechanical processes readily reduce it to a sufficiently fine state of division, and the fusion need not be continued for more than twenty minutes. It is true that the nickel crucible, in which the fusion is best carried out, is much attacked by the flux, but the presence of nickel does not interfere at all with the detection of the platinum metals, or of the other elements which are precipitated by hydrogen sulphide, nor does it interfere very seriously with the detection of the elements present in the precipitate produced by ammonium hydroxide or sulphide, since they can be separated from almost all of the nickel by treating the precipitate with dilute hydrochloric acid. It may be added that before finally adopting this procedure a few experiments were made on metallic iridium with the hope of effecting its solution by heating it to 200° in sealed tubes with bromine or with a mixture of bromine and concentrated hydrobromic acid, but the quantity dissolved was insignificant.

In concluding this chapter it is a pleasure to add that I have been ably assisted in this part of the work by Messrs. J. E. Ober, G. V. Sammet, and W. H. Whitcomb.

Procedure and Notes.

Procedure 1.—If the substance is a metal, treat it by P. 4.

If the substance is not a metal, proceed as follows:—Grind about 1.5 grm. in small portions in an agate mortar until it is so fine that no grit is perceptible when a little of it is rubbed between the fingers. Weigh out roughly about 1 grm. into a casserole, pour over it 10 c.c. HNO_3 (1.20), cover the dish, and digest the mixture on a water-bath for fifteen minutes, or as long as an action appears to be taking place. [If, however, it is thought necessary to test for the presence of osmium in the form of a salt, boil the substance in a distilling flask with HNO_3 , and collect and test the distillate by P. 13 and P. 14]. Then add 20 c.c. boiling water, and allow the residue to settle. [If a light coloured spongy mass of sulphur has separated, remove it by means of a rod or spatula]. Decant the liquid through a filter. If HNO_3 seemed to be slowly attacking the residue, digest it with a fresh portion of HNO_3 , dilute, and decant as before. Wash the residue with hot water twice by decantation, pouring the washings through the filter. Transfer the residue from the casserole, and filter to a platinum dish by rinsing with a little water. Decant or evaporate off the water. (Solution, P. 2; residue, P. 3).

Notes.

1. In order to secure the decomposition of difficultly decomposable substances by the following procedures, it is of fundamental importance that the substance be reduced to a literally impalpable powder, a result that can often be obtained only by the long-continued grinding of the substance in small quantities at a time.

2. One grm. of the substance is usually taken; for, since 1–2 m.grms. of almost any element can be detected by this system of analysis, with 1 grm. the presence of as little as 0.1–0.2 per cent can be determined, which is ordinarily sufficient. It is treated with the acid in a porcelain vessel because of the possible presence of chlorides, which would attack the platinum vessel which has to be used in the subsequent HF treatment (P. 3). The HNO_3 solution is decanted and the residue is washed for this same reason, and also because in many cases the elements which form insoluble fluorides, of which calcium is the most common, are thereby removed, so that the subsequent treatment with SiO_2 (P. 3) becomes unnecessary. The treatment in a distilling flask when osmium can be present as a salt is to avoid the loss of this element by volatilisation, as OsO_4 . See P. 13, N. 9.

3. If HNO_3 attacks the substance with separation of a white precipitate, the latter may consist of hydrated SnO_2 , Sb_2O_5 , SiO_2 , TiO_2 , GeO_2 , Nb_2O_5 , Ta_2O_5 , MoO_3 , or of BaSO_4 , PbSO_4 , SrSO_4 . Certain nitrates, especially $\text{Pb}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$, may also separate in crystalline form from the fuming HNO_3 ; but these dissolve upon adding water and heating to boiling. If a dense yellow decomposition product results, it probably consists of H_2WO_4 . A spongy mass which becomes pasty on boiling the solution is sulphur.

4. If a portion of the substance is not attacked by HNO_3 (1.20), it probably consists of one or more of the following substances:—The oxides and sulphates named in N. 3, the native or ignited oxides of aluminium, chromium, and zirconium, the peroxides of manganese and lead, the silicates and fluosilicates of many elements, sulphide of mercury, fluoride of calcium, the halides of silver, ferrocyanide of iron, carbon, silicon carbide.

Procedure 2.—Evaporate the HNO_2 solution (P. 1) as nearly to dryness as is possible without overheating the residue. Heat in a hot closet at 120° for one hour, or longer if the mass has not then become perfectly dry. (Residue, P. 5).

Note.

1. The evaporation to dryness and heating in the closet at 120° serve to dehydrate and make less soluble in HNO_3 silica and the hydroxides of the elements of

the tungsten and niobium groups, which may at first be dissolved by the HNO_3 . If the dry residue were strongly heated over a flame, mercury compounds might be volatilised, and iron, aluminium, and chromium oxides made insoluble.

Procedure 3.—Add to the residue insoluble in HNO_3 (P. 1) 5–10 c.c. pure concentrated (40 per cent) HF solution, and digest on a water-bath for fifteen minutes. Note whether complete solution takes place. Add 5 c.c. HNO_3 (1.42), and evaporate just to dryness. Cover the residue with HNO_3 (1.42), and again evaporate just to dryness. Add 10 c.c. HNO_3 (1.05), and heat to boiling.

If complete solution took place either on the addition of the HF, or if it occurs on the treatment with the HNO_3 (1.05), evaporate just to dryness a third time; then heat the dish for at least one hour in a hot closet at 120° .

If neither the HF nor the HNO_3 (1.05) produced a perfectly clear solution, evaporate the liquid just to dryness, loosen the particles from the dish, add 10 c.c. HNO_3 (1.42) and 1 grm. pure, ignited precipitated silica, cover the dish, and digest on a water-bath for three-quarters of an hour. Then evaporate the liquid just to dryness, and heat the dish for at least an hour in a hot closet at 120° . (Residue, P. 5).

Notes.

1. The HF used must leave no residue whatever after evaporation and gentle ignition, since otherwise foreign elements would be introduced. It must not contain H_2SO_4 in considerable amount, since otherwise BaSO_4 and PbSO_4 may be left undissolved on the subsequent treatment of the dehydrated residue with HNO_3 (P. 5) and HF (P. 6), and since some of the hydroxides of the niobium and tungsten groups may dissolve. The presence of H_2SO_4 in it may be detected by adding to 3 c.c. of it 10 c.c. HCl (1.03) or 20 c.c. HCl (1.02) and 1 c.c. 10 per cent $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ solution.

2. Whenever, as in the above procedure, it is directed to evaporate a solution "just to dryness," this should be done in such a manner as not to heat any portion of the dried residue much above 100° . This may be accomplished by heating upon a steam-bath, or more rapidly over a small flame, provided proper care be taken; in the latter case after the solution has been reduced to a small volume, the dish must be kept constantly in motion so that the heated parts of the sides as well as the bottom are always wet with liquid, and when nearly dry the dish must be often removed from the flame and shaken in the air, so that the final evaporation will take place at as low a temperature as possible.

3. If the substance is decomposed by HF with the separation of a white precipitate, this indicates the presence of lead, bismuth, lithium, magnesium, or of an element of the alkaline earth or rare earth group. If no such precipitate separates, it shows the absence in quantity as large as 1 m.grm. in the part of the original substance insoluble in HNO_3 , of lead, bismuth, calcium, and all the elements of the rare earth group. Since LiF , MgF_2 , SrF_2 , and BaF_2 are somewhat soluble, these precipitates separate only in the presence of considerable quantities of the elements—in the presence of, roughly, 5 m.grms. Li, 2 m.grms. Mg, 8 m.grms. Sr, 30 m.grms. Na, when 5 c.c. HF are used.

4. The HF solution must not be evaporated to dryness without the addition of HNO_3 ; for much titanium and tantalum would then volatilise as TiF_4 and TaF_5 . In the presence of HNO_3 , however, the loss of these elements is inconsiderable, undoubtedly owing to the fact that this acid decomposes their fluorides. In the evaporation with HF and HNO_3 there is no loss of mercury, arsenic, selenium, germanium, or antimony—the elements which volatilise to some extent out of a boiling concentrated HCl solution.

5. If complete solution takes place on the addition of HF, the three evaporations with HNO_3 remove the HF completely, even in the presence of the elements

titanium, niobium, tantalum, which have a great tendency to form complex fluorine containing acids. In that case, the treatment with SiO_2 can be dispensed with; and this is desirable, whenever practicable, both because it saves time at this point and because it makes it possible to determine immediately upon the treatment of the dehydrated residue with HNO_3 whether or not elements of the tungsten and niobium groups are present.

6. In case the HF precipitate consists of even large quantities (500 m.grms.) of PbF_2 , BiF_3 , LiF , MgF_2 , SrF_2 , or BaF_2 , or of a small quantity (less than 50 m.grms.) of CaF_2 , the two evaporations decompose it completely, so that these elements pass into solution on adding dilute HNO_3 , and the addition of SiO_2 is unnecessary.

7. If oxides of the tungsten and niobium groups are alone present in the first residue, these (with the possible exception of SnO_2) will yield a clear solution upon the treatment with HF (see P. 6, N. 1), but will again separate after the evaporations with HNO_3 ; in this case, in which HF, but not HNO_3 , yields a clear solution, it is, of course, also unnecessary to treat with SiO_2 .

8. When, however, CaF_2 or rare earth fluorides separate in considerable quantity on the addition of HF, it is not practicable to decompose them by repeated evaporations with HNO_3 alone. But the addition of SiO_2 and digestion with it and strong HNO_3 effect complete decomposition of all the fluorides (except ThF_4 , which may remain partially undecomposed as a dense crystalline powder). The SiO_2 combines with the HF that is liberated by the HNO_3 , and thus, in accordance with the Mass Action Law, enables the decomposition to become complete.

9. CaF_2 , even when present in considerable quantity after the two evaporations with HNO_3 , may yield a homogeneous, slightly milky colloidal solution upon the addition of dilute HNO_3 . This must not be mistaken for a true solution, the production of which alone warrants the omission of the SiO_2 treatment.

10. The SiO_2 used must leave no residue whatever upon treatment with HF and evaporation of the solution. It may be prepared by diluting commercial water-glass with three times its volume of water, adding HCl as long as precipitation continues, decanting, boiling the precipitate two or three times with water, drying it in a hot closet, heating it two or three times with HCl (1:20), washing it till free from acid, drying it in a hot closet, and finally igniting it.

11. The heating at 120° is necessary in order to make silica and the oxides of tin, tungsten, and tantalum entirely insoluble in HNO_3 . This is even more necessary after they have been dissolved by HF than when treated with HNO_3 alone. If the residue were overheated during the evaporations, other oxides, like those of iron, aluminium, and chromium, might not dissolve completely on the subsequent treatment with HNO_3 .

Procedure 4.—If the original substance is a metal, convert it into a form that offers as much surface as possible by grinding it in an agate mortar, hammering it in a "diamond" steel mortar, filing it with a fine steel file, shaving it with a knife, or converting it into borings with a drill. Weigh out roughly about 0.5 gm. into a casserole, pour over it, very gradually if a violent action occurs, 10 c.c. HNO_3 (1:20), cover the dish, and heat the mixture on the water-bath as long as any evolution of nitrous fumes occurs, adding more acid if the action is renewed thereby, or a little water if crystalline salts have separated. Then evaporate the liquid just to dryness, and heat the residue in a hot closet at 120° for an hour, or longer if the mass has not then become perfectly dry. (Residue, P. 5).

Note.

1. See P. 1, N. 3 in regard to precipitates that may separate during the HNO_3 treatment, and P. 3, N. 11 regard to the dehydration of the residue.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 15th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MESSRS. S. L. Courtauld, L. H. Durrans, and R. W. L. Clarke were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Ernest Barrett, B.Sc., 56, Elswick Road, Lewis- ham, S.E.; Percy Garratt Chamberlain, M.A., 3, Market Place, Rugby; Cecil Wyatt-Edgell, B.A., Cowrey Place, Exeter; O. Bertram Foy, 16, Burlington Road, Dublin; John Adam Watson, 8, Powis Gardens, Notting Hill, W.

A certificate has been authorised by the Council for presentation for ballot under By-law I. (3) in favour of Ram Chandra Mukerjee, B.A., of Jaipur, Rajputana, India.

The PRESIDENT announced that Dr. G. T. Morgan had found it necessary to resign the Editorship of the Society's publications, and the Council had appointed Dr. J. C. Cain to succeed him.

Attention was drawn to the fact that the Sixth International Congress of Applied Chemistry will be held in Rome, beginning on April 25th, 1906.

Of the following papers, those marked * were read:—

*53. "*The Interaction of well-dried Mixtures of Hydrocarbons and Oxygen.*" By WILLIAM ARTHUR BONE and GEORGE WILLIAM ANDREW.

The results of experiments carried out chiefly with mixtures of ethylene and oxygen, well dried by previous long contact with re-distilled phosphoric oxide, do not support the view that the presence of steam is essential to the combustion of a hydrocarbon. It was shown that an amount of desiccation which almost inhibits the combination of hydrogen and oxygen (electrolytic gas) at 525° does not appreciably retard the oxidation of ethylene. The authors therefore conclude that oxygen is directly active in hydrocarbon combustion.

*54. "*The Explosive Combustion of Hydrocarbons.*" By WILLIAM ARTHUR BONE and JULIEN DRUGMAN.

The authors showed, as the result of an exhaustive study of the explosive combustion of a number of different gaseous hydrocarbons, including paraffins up to butane and olefines such as ethylene, propylene, and the butylenes, that the theory of the preferential combustion of carbon completely breaks down when applied to hydrocarbon flames. The results of the research constitute a strong argument in favour of the view that there is no essential difference between the slow and rapid combustion of a hydrocarbon, and that explosive combustion probably involves the initial formation of unstable hydroxylated molecules, which subsequently undergo thermal decomposition into simpler products. Very striking differences as regards the composition of the end-products are obtained when explosive combustion occurs in the system $\text{C}_x\text{H}_y + x/2\text{O}_2$, according as the hydrocarbon is a paraffin or an olefine. In the case of a paraffin, there is always a separation of carbon and a large formation of steam, whereas in the case of the corresponding olefine there is no separation of carbon, and the cooled products consist almost entirely of carbon monoxide and hydrogen in accordance with the empirical equation $\text{C}_n\text{H}_{2n} + n/2\text{O}_2 = n\text{CO} + n\text{H}_2$. In the case of an olefine, it was shown that on reducing the proportion of oxygen much below that indicated by the expression $\text{C}_n\text{H}_{2n} + n/2\text{O}_2$, not only does carbon separate in the flame, but also a large formation of steam occurs, a result which is quite incompatible with the theory of the preferential combustion of carbon in hydrocarbon flames.

Comparative experiments on the explosion of mixtures corresponding to $\text{C}_2\text{H}_6 + \text{O}_2$, $\text{C}_2\text{H}_4 + \text{H}_2 + \text{O}_2$, and $\text{C}_2\text{H}_2 + 2\text{H}_2 + \text{O}_2$ respectively prove that the process cannot

be regarded as involving the primary dissolution of the hydrocarbon, followed by a distribution of the oxygen between free carbon and hydrogen.

Incidentally, it was shown that the affinity of hydrocarbons for oxygen at high temperatures is enormously greater than that of hydrogen, so that whenever mixtures of hydrocarbons and hydrogen react with a supply of oxygen less than is required to complete the initial combustion stages of the hydrocarbon, the latter is burnt almost to the entire exclusion of the hydrogen. Hence, in hydrocarbon flames, the initial stages of the oxidation of the hydrocarbon probably take precedence of all other chemical processes.

DISCUSSION.

Prof. SMITHELLS said that he was very ready to confess any mistake he might have made in giving currency to the idea of a "preferential oxidation" of carbon in the combustion of hydrocarbons. He admitted at once that the expression was not universally applicable, and he would endeavour in future not to use it without the necessary qualifications. He wished, however, to remind Fellows what the history of the matter really was. When he began to experiment with flames, he was under the conviction, which he believed was shared by chemists in general, that when a hydrocarbon was burned with a restricted supply of oxygen, carbon rather than hydrogen would remain unoxidised. That view lay at the root of the explanation of the luminosity of hydrocarbon flames then current. When, experimenting with the aerated flame of ethylene, he had found that the interconal gases contained a large quantity of free hydrogen and no unoxidised carbon, and when he had found this to be true of hydrocarbon flames in general, he felt that a complete revolution must be made in our views, and it was then that he used the expression preferential combustion of carbon. In describing chemical changes, it was customary to name the substances used and the substances ultimately obtained. Whatever transitory products might be formed, however the mechanism might be regarded, it was the custom to say, for example, that zinc and strong sulphuric acid give sulphur dioxide, zinc sulphate, and water. We might suppose that zinc first displaced hydrogen from the acid, and that the hydrogen reduced some more of the acid, or that the zinc was oxidised by the acid and the oxide then dissolved in more acid. Then, again, hydrogen sulphide and free sulphur were to some extent formed. In such an apparently simple reaction as this, we could affirm nothing with certainty about the actual mechanism. Therefore, we said simply that zinc and sulphuric acid give sulphur dioxide, water, and zinc sulphate. In like manner, it might be said that in the case of hydrocarbon flames burning with a restricted supply of oxygen the carbon was preferentially oxidised.

With regard to the probable course of the oxidation, he considered that Dr. Bone had made out a very strong case. It was undoubtedly possible that all the stages which the author had indicated might be passed through; he did not think the explanation presented great difficulties from the standpoint of the kinetic theory of gases. On the other hand, it was undoubtedly possible that the final condition of equilibrium might be reached in one bound, just as a stone under impulse might reach the foot of a hill in one bound instead of following the contour of the slope. It was a question of the balance of evidence. The most serious piece of experimental evidence he knew against Dr. Bone's view was, that in those parts of a flame where the partial combustion of hydrocarbons is taking place there is to be seen a spectrum which he believed to be only known where carbon and oxygen were uniting to form carbon monoxide. That spoke for a direct attack of the oxygen on the carbon. The solution of the question was one of extreme difficulty, and, as he had said, it involved the careful weighing of circumstantial evidence.

Having dealt, Dr. ARMSTRONG said, with Dr. Bone's work elsewhere, and being in agreement with him on the main issue, there were but few matters to which he need

refer. One of the most striking points brought before them was the incombustibility of hydrogen as compared with hydrocarbons—he thought that it would have to be recognised that hydrogen was not the active, attractive element it was commonly supposed to be in hydrogen compounds, but that more often than not it simply became pushed aside, as it were. The carbon appeared to be primarily the attractive element, and in this restricted sense Prof. SmitHELLS was justified in speaking of the preferential combustion of the carbon in hydrocarbons. As to the influence of moisture on the combustion of hydrocarbons, it was to be expected that a hydrocarbon-oxygen mixture would be much more sensitive to change than one of hydrogen and oxygen. Such questions must be regarded from the point of view of some consistent theory of chemical change; it would be very difficult to obtain direct experimental proof that conducting water was essential to the occurrence of the combustion. The view he had expressed twenty years ago in that room, that a mixture of hydrogen and oxygen alone would be found to be incombustible, was now accepted, however, and he did not hesitate to assert that it was necessary to extend the argument from hydrogen to hydrocarbons, but would not be surprised if another twenty years passed before it were recognised that a mixture consisting simply of a hydrocarbon and oxygen was incombustible.

Dr. BONE, in reply, remarked that the discussion had not elicited any definite criticism of the views he had advanced in the paper. His own position was simply this. In conjunction with Dr. Drugman, he had discovered certain facts which proved that preferential combustion of carbon did not take place in hydrocarbon flames, but which could be perfectly well explained on the supposition that hydroxylated or oxygenated molecules were initially formed. He had endeavoured to form a mental picture of the processes going on in the flame, but, beyond expressing the conviction that the oxygen is in some way actually incorporated with the hydrocarbon before the system breaks down into simpler products he did not wish to put forward any theory otherwise than as a working hypothesis.

*55. "*The Occurrence of Methane amongst the Decomposition Products of certain Nitrogenous Bases as a Source of Error in the Estimation of Nitrogen by the Absolute Method.*" By PAUL HAAS.

The gas collected over caustic potash in a Schiff's nitrometer during the estimation of nitrogen by the absolute method was found in the case of more than twelve different compounds to contain methane. The accumulation of this gas was prevented by replacing the copper oxide ordinarily used in such analyses by lead chromate, which effectually oxidises any methane formed.

DISCUSSION.

Mr. CARR remarked that the different results obtained when the base or its hydrochloride are burnt and the inhibitive influence of cuprous chloride confirmed the results obtained by Prof. Dunstan and himself. These experiments had shown that methane can only be burnt with great difficulty by passing it over strongly heated copper oxide. From the evidence now adduced he thought that the use of cuprous chloride in determinations of nitrogen by the absolute method should become general. More methane is obtained by the "carbon dioxide" method than by Frankland and Armstrong's vacuum method.

Mr. W. A. DAVIS stated that in 1896, shortly after the publication of Prof. Dunstan and Mr. Carr's results, he had found that 1-nitro-2-methoxynaphthalene gave abnormally high results for nitrogen estimated by the absolute method, and that the "nitrogen" collected was inflammable. The numbers obtained with the substance agree closely with those required for a dinitro-derivative, but the fact that normal results were obtained with the derived 1-amino- and 1-acetyl-amino-2-methoxynaphthalene clearly established the true nature of the compound. It was doubtful whether the formation of methane could be attributed to any special structure, but it seemed, under

exceptional conditions, to be associated with the presence of a methyl or methoxyl group.

Dr. BONE said that with regard to combustions over a hot surface of copper oxide, he had found that the rate of disappearance of hydrogen when electrolytic gas $2\text{H}_2 + \text{O}_2$, was circulated over copper oxide at 200° was only about 1/30th of the corresponding rate when a mixture of $2\text{H}_2 + \text{N}_2$ was employed. The oxygen in the electrolytic gas was condensed on the hot surface, forming a film which actually protected the copper oxide from the reducing action of hydrogen. Possibly other gases would be similarly condensed on the surface. He was not at all sure that the usual practice of using oxygen instead of air in ordinary combustion analyses over copper oxide was a good one.

56. "Studies on Comparative Cryoscopy. Part IV. The Hydrocarbons and their Halogen Derivatives in Phenol Solution." By PHILIP WILFRED ROBERTSON.

The hydrocarbons and their halogen derivatives are characterised by the fact that they give low molecular depressions, which decrease slowly with the concentration. This phenomenon appears to be intimately connected with the association of the solvent, as it is not exhibited to the same extent by the less associated substituted phenols, *o*-cresol, thymol, guaiacol, and *o*-nitrophenol.

It is also shown that benzene does not differ in behaviour from the other hydrocarbons examined, and hence its low molecular depression cannot be attributed to the formation of a solid solution, as Bruni endeavours to prove (*Gazzetta*, 1898, xxviii., [i.], 249). By employing van Bijlerts' method, his results show that the benzene forms a 30 per cent solid solution in the phenol. From this it is concluded that van Bijlerts' method is not always trustworthy, and, moreover, it is not justifiable to assume the existence of a solid solution when the observed molecular depression differs only slightly from the theoretical.

57. "The Displacement of Acid Ions." (Part I.). By ALFRED FRANCIS JOSEPH.

The author described his investigations on the quantitative action of hydrochloric acid on the nitrates of potassium, sodium, and strontium, and of nitric acid on the corresponding chlorides. An equivalent of the salt in aqueous solution is mixed with x equivalents of the acid, the mixture evaporated to dryness on the water-bath, and the proportion of chloride in the residue determined by titration with standard silver nitrate solution.

If the quantity of salt transformed be y , then it is found that the equation $y = a \log_{10} x + b$ holds good over a considerable range of values of x , a and b being constants depending on the particular acid and salt used. These constants increase and decrease simultaneously with the ratio of the solubilities of the two salts concerned in the transformation. It was found that to transform half the nitrate into chloride by one evaporation with hydrochloric acid requires about 1.5 equivalents of acid in the case of sodium nitrate, 2.9 for potassium nitrate, and 12 for strontium nitrate.

On the other hand, to transform nine-tenths of the chloride into nitrate requires 1.6 equivalents of nitric acid in the case of sodium chloride, 1.4 for potassium chloride, and 1.05 for strontium chloride.

58. "Additive Compounds of Arylamines with Aromatic Nitro-derivatives." By CHARLES LORING JACKSON and LATHAM CLARKE.

NOTE.—The investigations on additive compounds of trinitrobenzene with amines formerly described (*Ber.*, 1904, xxxvii., 176), and in this paper were undertaken before a copy of J. J. Sudborough's second paper (*Trans.*, 1903, lxxxiii., 1334) had been received by the authors, who thereupon discontinued their experiments.

The following additive compounds have been prepared by the authors in addition to those already described (*Ber.*, 1904, xxxvii., 176).

4 : 6 - Dibromo-1 : 3 - dinitrobenzene dimethylaniline, $2\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)_2, \text{C}_6\text{H}_5\cdot\text{NMe}_2$, which is precipitated as a

heavy red oil. When alcohol is added to a solution of the nitro-compound in an excess of dimethylaniline, it quickly solidifies to short deep red prisms melting at 50° .

0.3487 gave 0.3373 AgBr. Br = 41.12 .

0.1762 „ 0.1705 AgBr. Br = 41.16 .

$\text{C}_{20}\text{H}_{15}\text{O}_8\text{N}_5\text{Br}_4$ requires 41.39 per cent.

The compound is extremely unstable, and readily loses dimethylaniline when exposed to the air.

4-Chloro-1 : 3 : 5-tribromo-2 : 6-dinitrobenzene dimethylaniline, $\text{C}_6\text{ClBr}_3(\text{NO}_2)_2, 2\text{C}_6\text{H}_5\cdot\text{NMe}_2$, obtained in the same way as the preceding compound, crystallises in slender yellow needles, and melts at 105° .

0.086 gave 0.0889 AgCl and AgBr; Cl + Br = 40.25 .

$\text{C}_{20}\text{H}_{11}\text{O}_8\text{N}_5\text{Cl}_2\text{Br}_6$ requires Cl + Br = 40.43 per cent.

The following compounds give red colourations with dimethylaniline; in certain cases the colour is removed by the addition of solvents, and in no case has a definite crystalline additive compound been isolated. Nitrobenzene, *a*-nitronaphthalene, *o*-nitrophenol, *m*-dinitrobenzene, 4-bromo-1 : 3-dinitrobenzene, 4 : 6-di-iodo-1 : 3-dinitrobenzene. 1 : 3 : 5-trichloro-2 : 4-dinitrobenzene, 4-bromo-3 : 5-dinitrobenzoic acid (which yields a salt melting at 120 – 125°), 4-ethoxy-3 : 5-dinitrobenzoic acid, 4-*iso*-amyl-3 : 5-dinitrobenzoic acid, and picric acid.

Methylaniline and *s*-trichlorotrinitrobenzene yield an unstable additive compound, which crystallises in red plates, melting at about 78° ; it becomes colourless when exposed to the air or when washed with ether, chloroform, or acids.

Several of the compounds of toluidines with trinitrobenzene and trinitrotoluene have been prepared (compare, Hepp, *Annalen*, 1882, ccxv., 344; Noelting and Sommerhoff, *Ber.*, 1906, xxxix., 76). The compounds with trinitrotoluene are much less stable than those with trinitrobenzene.

The additive compound of *p*-toluidine and trinitrotoluene, which Sommerhoff could not obtain, may be prepared by fusing a mixture of the two components, adding a very small amount of toluene, and allowing to cool; it crystallises in dark red needles melting at about 68° .

0.2845 gave 41.4 c.c. of moist nitrogen at 20° and 768 mm. N = 16.82 .

$\text{C}_{14}\text{H}_{14}\text{O}_6\text{N}_4$ requires N = 16.76 per cent.

s-Trichlorotrinitrobenzene and pyridine form an extremely unstable additive compound, $\text{C}_6\text{Cl}_3(\text{NO}_2)_3, \text{C}_5\text{H}_5\text{N}$, which crystallises in slender red crystals.

0.1232 gave 0.1224 AgCl. Cl = 24.56 . $\text{C}_{11}\text{H}_5\text{O}_6\text{N}_4\text{Cl}_3$ requires 26.87 per cent.

When kept for a short time, this substance sets to a black resin.

59. "Influence of Substituents in the Trinitrobenzene Molecule on the Formation of Additive Compounds with Arylamines." By JOHN JOSEPH SUDBOROUGH and NORMAN PICTON.

The formation of additive compounds between *a*- or *β*-naphthylamine and *s*-trinitrobenzene derivatives is completely inhibited by the introduction of three methyl-, two methoxy-, or three bromo-radicles into the trinitrobenzene molecule. *s*-Trichlorotrinitrobenzene, however, is still capable of combining with *a*-naphthylamine. Various additive compounds are described.

The compounds derived from the naphthylamines and chloro-derivatives of the di- and tri-nitrobenzenes readily lose hydrogen chloride, yielding condensation products of the type of picryl-*β*-naphthylamine, $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$. Several compounds of this type have been examined, and the following points established:—1. Most of the compounds exist in two distinct modifications, namely, a sulphur-yellow and a bright red variety. These may be mutually transformed one into the other by simple methods. 2. They form mono-potassium salts which are readily hydrolysed by water. 3. They do not yield acetyl deriva-

tives. 4. Some form extremely unstable additive compounds with arylamines. 5. It has not been found possible to replace the one arylamino-group, $\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ for example, by another, such as $\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$.

60. "The Relations between Absorption Spectra and Chemical Constitution. Part IV. The Reactivity of the Substituted Quinones." By ALFRED WALTER STEWART and EDWARD CHARLES CYRIL BALY.

The reactive power of carbonyl groups in quinones has been shown by Kehrman (*Ber.*, 1888, xxi., 3315; *Journ. Prakt. Chem.*, 1889, [2], xxxix., 399; xl., 257) to be greatly influenced by the replacement of the hydrogen atoms of the quinone nucleus by methyl radicles or halogen atoms. This has hitherto been explained on the assumption that such substituents sterically hinder the reactions of the carbonyl group in the ortho-position to which they lie. It appeared to the authors that a better explanation might be found in the influence of the substituents on the isorropic process in which the quinone carbonyls are concerned.

An examination was made of the absorption spectra of the following quinones:—*p*-Benzoquinone, *tolu*quinone, *p*-xyloquinone, thymoquinone, chlorobenzoquinone, bromobenzoquinone, 2:6-dichlorobenzoquinone, trichlorobenzoquinone, trichlorotoluquinone, dibromothymoquinone, and dichlorothymoquinone; and from these spectra the following facts may be deduced:—(1) Benzoquinone has an isorropic band of long persistence, and shows no sign of benzenoid structure; (2) the introduction of methyl radicles or of halogen atoms tends to diminish the persistence of the isorropic band, and to produce in the spectrum a benzenoid band, the change being greater with chlorine than with methyl; (3) the benzenoid character of the compound is intensified in proportion to the decrease in the isorropic band.

From these facts the following conclusions may be drawn:—Benzoquinone exists almost entirely in the quinonoid form. Toluquinone, while existing to a great extent in the quinonoid form, possesses certain characteristics of benzene, and probably vibrates in a manner similar to that in which the benzene molecule oscillates. Chlorobenzoquinone, although still possessing certain quinonoid properties, is in a state of vibration approximating more closely to the intra-molecular motions of benzene. Trichlorobenzoquinone, in which the isorropic process is practically non-existent, vibrates in a manner closely resembling the vibrations of the benzene ring.

Now Kehrman has shown that the introduction of methyl radicles or halogen atoms hinders the formation of quinonoximes, and the amount of hindrance observed by him is in complete accord with the change in character from the quinonoid to the benzenoid type which is proved by the spectroscopic evidence. In their previous papers (*Proc.*, xxii., p. 33), the authors showed that in order to bring about the isorropic process the quinonoid structure had first to be produced. As the reactivity of the carbonyl group depends on the isorropic process, it is evident that the benzenoid character of the compounds examined is alone sufficient to explain their non-reactivity, without introducing the question of a purely hypothetical "steric hindrance." The facts now submitted, in conjunction with those already communicated to the Society, tend to show that there is no necessity for the assumption of any such purely mechanical causes underlying the hindrance to chemical reactions.

61. "The Constitution and Properties of Acyl Thiocyanates." By JOHN HAWTHORNE.

It has been shown (Dixon and Hawthorne, *Trans.*, 1905, lxxvii., 468) that when acetyl "thiocyanate" interacts with aniline, two changes occur simultaneously:—(1) Double decomposition, the sulphur appearing as thiocyanic acid, $\text{AcSCN} + \text{PhNH}_2 = \text{HSCN} + \text{AcNHPh}$; (2) addition, the sulphur now exhibiting thiocarbimide functions, $\text{AcNCS} + \text{PhNH}_2 = \text{AcNH}\cdot\text{CS}\cdot\text{NHPh}$. At low temperatures the former reaction predominates, and at high temperatures the latter.

It has now been shown that, besides temperature, two other factors may have an influence on the course of the interaction between an acyl "thiocyanate" and a base:—

(1) The nature of the base presented, and (2) the nature of the acidic radicle of the "thiocyanate." The results are recorded of experiments made at various temperatures on the systems *o*-toluidine—acetyl "thiocyanate" and aniline—propionyl "thiocyanate," from which it appears (1) that *o*-toluidine causes a great increase of the thiocarbimide functions of acetyl "thiocyanate" as compared with aniline, and (2) that, towards aniline, acetyl and propionyl "thiocyanates" behave very nearly alike.

Since in all the above reactions acetyl "thiocyanate" behaves towards a given base as if it were a mixture of acetyl thiocyanate and acetylthiocarbimide in proportions depending on the temperature, a series of determinations of the molecular refraction of the pure substance was carried out. Within the limits of temperature examined, this value was practically constant, the mean, 45.9, as deduced from the formula $M = \frac{(\mu - 1)m}{d}$, being inconsistent with the value required for a compound having the structure $\text{Ac}\cdot\text{S}\cdot\text{C}\cdot\text{N}$, but agreeing closely with that corresponding to $\text{Ac}\cdot\text{N}\cdot\text{C}\cdot\text{S}$.

62. "A Mode of Formation of Aconitic and Citrazinic Acids and their Alkyl Derivatives, with Remarks on the Constitution of Aconitic Acid." By HAROLD ROGERSON and JOCELYN FIELD THORPE.

By the condensation of the sodium derivative of ethyl cyanoacetate with ethyl oxalacetate, ethyl α -cyanoaconitate, $\text{CN}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, is produced. This ethyl salt on hydrolysis with acid hydrolysing agents is converted into aconitic acid, whilst with alkaline hydrolytic agents it is transformed into citrazinic acid. Alkyl derivatives of these compounds are formed when alkyl derivatives of ethyl α -cyanoaconitate, prepared either by the direct alkylation of this substance or by the condensation of the sodium derivative of ethyl cyanoacetate with alkyl derivatives of ethyl oxalacetate, are hydrolysed. It was shown that aconitic acid, like glutamic acid, has a symmetrical structure, and that α -methyloaconitic and γ -methyloaconitic acids are tautomeric.

(To be continued).

THE NATIONAL PHYSICAL LABORATORY.

THE Annual Meeting of the General Board of the National Physical Laboratory took place at Bushy House on Friday, March 16, 1906. There were present, in addition to the Chairman, Lord Rayleigh, the following among others:—Sir John Wolfe Barry, Mr. Beilby, Mr. Kempe, Mr. R. K. Graye, Col. Crompton, Mr. Hadfield, Mr. Gavey, and Mr. Howard.

In opening the proceedings Lord RAYLEIGH referred to the great loss the Laboratory had sustained by the deaths of Sir E. Carbutt and Sir B. Samuelson.

The Report of the Executive Committee for 1905 was presented and approved for presentation to the Royal Society, on the motion of Sir J. WOLFE BARRY, seconded by Mr. DAVID HOWARD. The Scheme of Work for 1906 was also approved. The Report showed progress in all directions.

Some fourteen Scientific papers of importance have been published officially, while members of the staff have contributed nine others to various journals.

The second volume of Collected Papers is in course of preparation.

The Scheme of Work for 1906 includes a research into the resistance of materials of construction to impact, the continuation of the wind pressure, and steam researches, the completion of the work with the Ampère balance, and some experiments of great interest on the effect of the continued application of high pressure to insulators. In the

Metallurgical Division a research into the properties of aluminium-bronze promises interesting results.

The Report announced the intention of the Government, communicated to the Royal Society in December last, to grant a sum of £5000 for buildings during the year, and the increase of the Annual Grant by £500. It referred also to the very successful meeting in the House of Commons last August, under the Chairmanship of Mr. Haldane, which led up to a petition signed by 150 Members of the House asking that the grants should be increased, and the Chairman was able to announce that the Chancellor of the Exchequer had recently intimated his intention of making the building grant for the year £10,000 instead of £5000 as originally contemplated.

It was also stated that the Goldsmiths' Company had very generously made a donation of £1000 with the request that it should be devoted to some specific object.

The very cordial thanks of the Board were voted to the Chancellor of the Exchequer, Mr. Haldane, Sir J. Lawrence, Sir J. Brunner, and the other gentlemen who had interested themselves in the House of Commons petition, and also to the Goldsmiths' Company.

The Director gave an account of the proposed additions to the buildings rendered possible by the increased grant, and explained the plans which had been prepared by the Building Committee. The suggestion that the work of erecting these buildings should now be pressed forward was cordially welcomed, and at a meeting of the Executive Committee held later power was given to the Building Committee to take the necessary steps.

The Board then adjourned to inspect the Laboratory and to view the new Electrical Buildings. These are now approaching completion. They have been erected by Messrs. Mowlem and Co., at a cost of about £8000, to the design of Messrs. Mott and Hay, who very kindly gave their services, while with marked generosity Messrs. Mowlem's tender was based on the cost price of the buildings.

It is hoped that they may be opened on June 25th, on the occasion of the visit of the foreign guests of the Institution of Electrical Engineers. In view of this ceremony the invitations on Friday were restricted to Members of the Board and their personal friends; the usual annual gathering of friends of the Laboratory being postponed until June.

NOTICES OF BOOKS.

Utilisation of Nitrogen in Air by Plants. By THOMAS JAMIESON. Aberdeen: Agricultural Research Station. 1905.

THE author of this book claims that he has made a discovery which must be recognised as of the greatest importance—namely, that plants in general possess the power of absorbing nitrogen from the atmosphere. Cereals and grasses have the same power, though to a less extent than other plants. He asserts that the opposite conclusion was based upon experiments performed on very small and weak plants, grown under such unnatural conditions that full vigour was not attained. He first brings forward arguments to disprove the tubercle theory, and then proceeds to state the reasons which have led him to adopt the conclusion above referred to. He bases his views upon the discovery of specialised structures to which he gives the name "albumen generators." These structures are found on the softest parts of the younger leaves and leaf stalks of many families, among which may be mentioned the weeds *Spergula*, *Stellaria*, and *Urtica*, and many cultivated plants. The argument rests entirely upon the discovery of the presence of albumen (detected by means of iodine, cupric sulphate, and mercury nitrate) in the tip of the hair-like structure and its subsequent discharge into the leaf; and apparently no tests were arranged to demonstrate the

source of the nitrogenous compound. The author suggests practical applications, and describes some trials which have been made to show that the legumes are not alone in benefiting the after crop, rape being suggested as the most suitable plant to grow as a nitrogen provider; but the facts given are quite insufficient to prove the theory.

Electro-chemistry of Organic Compounds. By Dr. WALTHER LÖB. Authorised Translation by H. W. F. LORENZ, A.M., Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1906.

THE second American edition of Dr. Löb's work has been prepared from the third German edition, which the author published about a year ago, and which was greatly enlarged and thoroughly revised. The new matter, which attains the same high degree of excellence as was a marked feature of the earliest edition, includes some sixty pages on Electro-thermic Processes and the Silent Electric Discharge, in which a brief *résumé* of the subject is given. A new chapter on Electric Endosmose or cataphoresis describes the effects of this phenomenon and touches upon its practical importance and application. Considerable alteration has been made in the arrangement of the text, the general theory of electrolysis being treated in an introductory section, in which the theoretical aspects of organic electro-chemistry are discussed more fully than in the old edition, while some space is devoted to the discussion of methodics, although the author has not aimed at providing a laboratory guide, and merely wishes to indicate some of the more important details of the practical work in such a way as to enable the reader to understand thoroughly the various methods commonly employed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 9, February 26, 1906.

Difficulties of Estimation of Carbon Monoxide in Gaseous Mixtures.—Armand Gautier and M. Clausman.—The estimation of small traces of carbon monoxide in a mixture of such gases as ethylene, methane, nitrogen, hydrogen, oxygen, &c., is attended with great difficulties. The authors point out a number of these difficulties and various methods of overcoming them.

Addition of Hydrochloric Acid to Isobutylene Oxide, $(\text{H}_3\text{C})_2\text{C}(\text{O})\text{CH}_2$.—Louis Henry.—The author's researches prove beyond doubt that there do exist two distinct isobutylenic compounds, due to the considerable functional difference existing in the carbon atom, owing to the presence or absence of hydrogen. The existence of these two chlorohydrins being established, the author is proceeding to prove that hypochlorous acid, $(\text{HO})\text{Cl}$, can be fixed on to isobutylene, $\text{H}_3\text{C} > \text{C} = \text{CH}_2$.

Lævo-lactic Acid.—E. Jungfleisch and M. Godchot.—The authors describe the preparation of pure crystalline *l*-lactic acid, and investigate its properties. They find that solutions of *l*-lactic acid when charged with *l*-lactylactic acid can at the same time give solutions of zinc salts of the two acids, zinc *l*-lactylactate having a dextro-rotatory power considerably greater than that of zinc *l*-lactate. These facts, which are analogous to those which have been observed for *d*-lactic acid, may have an influence on the exact determination of the nature of lactic acids resulting from numerous microbe fermentations.

MEETINGS FOR THE WEEK.

- MONDAY, April 2nd.**—Society of Arts, 8. (Cantor Lectures). "Fire, Fire Risks, and Fire Extinction," by Prof. Vivian B. Lewes.
- Royal Institution, 5. General Monthly Meeting.
- Society of Chemical Industry, 8. Election of Officers and Committee. "Rapiness in Flour and Bread, and its Detection and Prevention," by E. J. Watkins. "The Rösse-Herzfeld and Sulphuric Acid Methods for the Determination of the Higher Alcohols" (a Criticism), by V. H. Veley.
- TUESDAY, 3rd.**—Royal Institution, 5. (Tyndall Lectures). "The Influence of Geology on Scenery," by John E. Marr, F.R.S., &c.
- WEDNESDAY, 4th.**—Society of Arts, 8. "Ramie and its Possibilities," by Mrs. Ernest Hart.
- THURSDAY, 5th.**—Royal Institution, 5. "Internal Combustion Engines" (with Experimental Illustrations), by Prof. Bertram Hopkinson, M.A., &c.
- Chemical, 8.30. "An Improved Apparatus for Measuring Magnetic Rotations and obtaining a Powerful Sodium Light," by W. H. Perkin, sen. "Rusting of Iron," by G. T. Moody. "Determination of Carbon in Soils," by A. D. Hall, N. H. J. Miller, and N. Harmer. "The Electrolysis of the Salts of $\beta\beta$ -Dimethylglutaric Acid," by J. Walker and J. K. Wood. "Bromo- and Hydroxy-derivatives of $\beta\beta\beta\beta$ -Tetramethylsuccinic Acid," by J. K. Wood. "Some New Urthoxyene Derivatives," by G. Stallard. "New Solvent for Gold," by J. Moir. "Molecular Condition in Solution of Ferrous Oxalate" (a Correction), by S. E. Sheppard and C. E. K. Mees.
- FRIDAY, 6th.**—Royal Institution, 9. "The Physical Basis of Life," by William Bate Hardy, F.R.S., &c.
- SATURDAY, 7th.**—Royal Institution, 3. "The Corpuscular Theory of Matter," by Prof. J. J. Thomson, F.R.S., &c.

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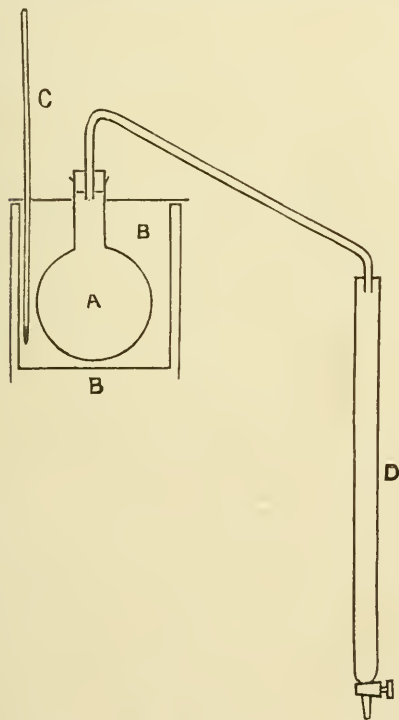
VOL. XCIII., No. 2419.

ROSIN SIZE ANALYSES.

By CLAYTON BEADLE and HENRY P. STEVENS.

ROSIN is the residue left in the retort when crude turpentine is distilled with the object of obtaining "oil" or "spirits of turpentine." It is not to be expected that the separation of the rosin from the spirits of turpentine would be complete, and a trace of the latter remains behind in the rosin—the quantity varying with the form of plant used for distilling and the temperature to which the crude turpentine is heated.

When the rosin is used for making rosin size, it will therefore contain a residue of crude turpentine. In the manufacture of rosin size this turpentine may be partially driven off or the greater part retained, according to the system employed; and the final product, the rosin size, may also contain larger or smaller quantities of turpentine.



DIRECT DETERMINATION OF MOISTURE IN ROSIN SIZE APART FROM OTHER VOLATILE BODIES.

A, Flask heated in asbestos air-bath, B, provided with thermometer, C. Water and other volatile substances collect in the burette D, where the volume is read off.

To estimate the moisture in rosin size, it is usual to dry down a small quantity in a flat dish or clock-glass kept at a constant temperature of 100° to 110° C.; the loss in weight is taken to represent the moisture. Should, however, the size contain a large proportion of turpentine, part or whole of this may be driven off and lost, and will therefore be included as moisture.

With the object of testing this point, a very thorough analysis was made on a sample of rosin size by different methods, and the results compared. We are indebted to

Mr. G. W. Ross for carrying out these experiments, which are recorded below. The close agreement between the results obtained by different methods speaks for the accuracy of the determinations. The moisture was determined by the following methods:—

1. As suggested by Mr. H. Ardleter, attempts were made to estimate the water directly by distillation. The method adopted by us was the following:—A quantity of size was weighed into a glass flask, which was then placed in an air-bath and connected with a condensing tube, the end of which was bent over, dipping an inch or so into a burette graduated in tenths of a c.c. The burette, before the experiment, was filled up with water, which was then allowed to run out until the 50 c.c. mark at the bottom of the tube was reached. The flask was then gradually heated in the air-bath, and the distillate which condensed in the tube collected in the burette. The heating was gradual, and the distillation took half an hour to an hour. When nothing further distilled over, the volume of the distillate was read off. In each case a small quantity of turpentine was found floating on the surface of the water, and the volume of this was read off separately.

2. At the end of the experiment the flask was allowed to cool and then re-weighed, thus giving the loss in weight by difference. This loss would represent moisture, turpentine, and any gaseous substances driven off.

3. The loss by difference was checked by a test carried out in the ordinary method by drying down at 100–110° C. a weighed quantity of the size in a clock-glass.

4. A complete analysis was made of the size, including the total rosin, total soda, other mineral matter, and turpentine. The remainder will represent moisture "by difference." The figures obtained were as follows:—

METHODS 1 and 2.

Experiment.	Volume of water distilling over.	Loss in weight of contents in flask.
	Per cent.	Per cent.
1.	38·5	39·8
2.	39·8	39·4
3.	38·0	39·4
4.	38·7	39·6
Mean of all four experiments . .	38·75	39·55

METHOD 3.

Loss of weight by drying down in a clock-glass at 100–110° C. 39·5

METHOD 4.—Rosin by Extraction with Ether.

Experiment.	Total.
	Per cent.
1.	55·8
2.	56·3
3.	56·0
Mean of three experiments . .	56·03

Complete Analysis.

Total rosin	56·03
Total soda (Na ₂ O)	3·55
Turpentine	0·34
Other mineral matter	0·24
Moisture (by difference)	39·84

100·00

It will be seen that the amount of turpentine distilled over is very small—on an average only 0·34 per cent. The figures for moisture obtained by different methods agreed very well among themselves. The figures obtained in Method 1 vary more among themselves than some of the others, as there is a limit of accuracy in the direct estimation of the moisture, as it must be remembered, in the first place, that an ordinary burette cannot be read to less than one-twentieth of a c.c.; and then, again, it is not

practicable to take very large quantities of the size. The amounts actually taken were as follows:—

Experiment 1	37.70	grms. taken for analysis.
" 2	36.27	" " "
" 3	14.61	" " "
" 4	54.76	" " "

There is another practical difficulty in estimating the moisture directly in this manner. The water and turpentine distilling over have to pass through a condensing tube before reaching the burette where they are measured. When a dry condensing tube is taken to start with, a certain amount of moisture remains adhering to the sides. To get this into the burette the tube must be carefully warmed, so as to increase the mobility of the water and allow it to run down into the burette. A small loss of moisture under these circumstances is unavoidable. In two of these experiments another method was adopted. The condensing tube was rinsed out with water before starting the distillation, on the assumption that it would contain at the start of the experiment as much water as it would retain at the end. It is curious to note that the turpentine seems to come over with the first drops of water, although its boiling-point is considerably above that of water.

Turpentine is a mixture of various substances, and its main constituent, "pinene," boils at 155–156° C.; that is, considerably above the boiling-point of water. The quantity of turpentine-like bodies obtained was too small to allow of further examination. The turpentine was estimated by measuring its volume and calculating its weight by allowing for its density (0.86 to 0.87).

The results obtained are, taken as a whole, very concordant. The figure for moisture (39.5), obtained by drying down on a watch-glass in the ordinary method, agrees very well with that obtained in a similar manner by the mean loss in the weight of the flask, viz., 39.55. The other figures are almost as close, 38.75 being the mean percentage for the volume of water distilled over, and 39.84 for moisture by difference on the complete analysis. This latter figure is, perhaps, higher on account of the total rosin being possibly too low; it is always difficult to extract the last portions of resin with ether unless the operation be repeated several times with fresh portions, due to the solubility of ether in water. We may conclude that, so far as the results go, no sensible error is produced by determining the moisture by drying down a small quantity in an open vessel, such as a clock-glass; but this might not hold with samples containing more turpentine than that used for these experiments. This point can only be settled by subjecting a number of samples of rosin size from different sources to distillation and other tests, as above.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution after Easter:—Professor G. Baldwin Brown, two lectures on "Greek Classical Dress in Life and in Art"; Professor William Stirling, three lectures on "Glands and their Products"; Dr. O. Chalmers Mitchell, two lectures on "The Digestive Tract in Birds and Mammals"; Rev. J. P. Mahaffy, two lectures on—(1) "The Expansion of Old Greek Literature by Recent Discoveries," (2) "The Influence of Ptolemaic Egypt on Græco-Roman Civilisation"; Professor William J. Sollas, three lectures on "Man and the Glacial Period"; Professor Charles Waldstein, three lectures on "English Furniture in the Eighteenth Century"; Professor Sir James Dewar, two lectures on "The Old and the New Chemistry"; and Professor W. Macneil Dixon, two lectures on—(1) "The Origin of Poetry," (2) "Inspiration in Poetry." The Friday Evening Meetings will be resumed on April 27, when Professor John W. Gregory will deliver a Discourse on "Ore Deposits and their Distribution in Depth." Succceeding Discourses will probably be given by the Hon. Charles A. Parsons, Professor J. H. Poynting, Professor Arthur Schuster, Mr. Leonard Hill, Professor H. Moissan, Professor Sir James Dewar, and other gentlemen.

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

PART I. (continued).—PREPARATION OF THE SOLUTION
(INCLUDING THE DETECTION OF OSMIUM, SILVER,
AND LEAD).

By ARTHUR A. NOYES.

(Continued from p. 149).

Procedure 5.—Loosen the dehydrated residue (P. 2, 3, or 4) from the dish, and rub it to a fine powder with a pestle; add to it 5 c.c. HNO_3 (1.20), or 10 c.c. if it seems necessary, cover the dish, and heat on a steam-bath for ten minutes. Note whether there is any residue whatever. If no residue can be seen, rub the sides of the dish with the rubber-covered end of a glass rod, and allow the liquid to stand three or four minutes. If there is a crystalline residue of nitrates, add enough water to dissolve it, and note whether an amorphous residue remains. Dilute with 20 c.c. water, and heat to boiling. If the substance was a non-metallic one, unite at this point the two portions (treated by P. 2 and P. 3), unless it is desired to know their constituents separately. Decant the solution through a washed filter, retaining in the dish as much of the residue as possible. If the residue is large in amount, heat it again with 5 c.c. HNO_3 (1.20), dilute with water, and decant the solution through the same filter. Wash the residue with HNO_3 (1.05), decanting the washings through the filter, and transfer it to a platinum dish. (Residue, P. 6; solution, P. 51).

Notes.

1. If SiO_2 has not been added, important conclusions can be drawn in regard to the absence of certain elements in the substance when nothing whatever remains undissolved upon treating the dehydrated residue with HNO_3 (1.20). The fact must not be overlooked, however, that in the dehydrated form even a very small residue or slight turbidity may correspond to an appreciable quantity of an element. A perfectly limpid solution and one that does not deposit any sediment whatever after a few minutes' standing must be obtained, if such conclusions are to be drawn. Moreover, it should be noted whether such a solution results before diluting the HNO_3 (1.20) with water (or after diluting it with as little water as suffices to dissolve crystalline nitrates); for any residue is more difficult to recognise in a large volume of liquid.

In case no residue whatever remains, it shows the absence of silicon, tin, niobium, and tantalum in quantity as large as 1 m.grm.; of antimony in quantity as large as 2 m.grms., except when an organic hydroxy-acid is present, and of tungsten in quantity as large as 1 m.grm., except when phosphoric or arsenic acid or an organic hydroxy-acid is present. It also indicates the probable absence of titanium in quantity as large as 1 m.grm., except when zirconium is present.

Organic hydroxy-acids, like tartaric, lactic, and citric acids, dissolve Sb_2O_5 and H_2WO_4 with great readiness. H_2WO_4 also dissolves very readily when H_3PO_4 or H_3AsO_4 is present, owing to the formation of complex acids. The presence of arsenic, phosphoric, and organic acids is detected in the course of the subsequent procedure. Boric acid does not increase the solubility of any of the oxides of the tungsten and niobium groups. Moreover, it will not be present if the substance has been treated with HF; for even 1 m.grm. H_3BO_3 volatilises completely upon evaporation with 5 c.c. of this acid and 5 c.c. HNO_3 (1.42). Even 500 m.grms. of titanium may dissolve completely in the HNO_3 when much zirconium (500 m.grms.) is present.

2. If SiO_2 has been added, the presence or absence of the tungsten and niobium groups cannot be determined

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until the residue insoluble in HNO_3 has been treated with HF, the solution evaporated with H_2SO_4 and NH_4OH and $(\text{NH}_4)_2\text{S}$ added (P. 6 and Part II.).

3. The residue insoluble in HNO_3 may contain, in addition to the oxides of the elements named in N. 1, the following substances:— MoO_3 , when molybdenum is present in quantities over 100 m.grms., or when tungsten or tin is also present; GeO_2 , when over 30 m.grms. Ge are present; Bi_2O_3 , when much antimony is also present; SeO_2 and TeO_2 , when much tin or antimony is also present; ThF_4 , when much thorium is present in the residue treated with HF; the phosphates and arsenates of tin, titanium, zirconium, and thorium, and the vanadate of tin, when the components of these substances are simultaneously present. The residue may also contain certain undecomposed substances (named in P. 6, N. 2) which are not attacked by either HNO_3 or HF.

4. Of the elements named in N. 3 which may under the specified conditions be present in the residue insoluble in HNO_3 , the following ones always pass into the HNO_3 solution in considerable proportion when large quantities of them are present:—Molybdenum, bismuth, selenium, tellurium, zirconium, thorium, vanadium, germanium. This is also true of titanium (N. 1). Furthermore, a small quantity of antimony (1–2 m.grms.) dissolves. Phosphoric, arsenic, and vanadic acids are dissolved completely when tin, titanium, and zirconium are absent.

5. Aside from the elements named in N. 1, and under the specified conditions aside from those named in N. 3, no others are retained in the residue insoluble in HNO_3 in important quantity, as far as is known. Even the elements bismuth, tellurium, zirconium, and thorium, whose salts are readily hydrolysed, dissolve completely when present alone in quantities up to 500 m.grms. This is also true of zirconium, even when 500 m.grms. Ti are present. The elements iron, aluminium, and chromium, whose oxides are made insoluble by ignition, dissolve completely when the residue has been heated only to 120° , at any rate upon the second digestion with HNO_3 (1:20). Of the element gold, if originally present as chloride, only the small portion reduced by dust from the air is left in the residue.

6. Whenever it is directed, as at the end of this procedure, to "wash" a residue or precipitate, it is understood, unless otherwise stated, that this operation is to be continued until the washings will give no test for some substance known to be present in the solution in considerable quantity.

Procedure 6.—Support the filter containing some of the residue insoluble in HNO_3 (P. 5) in a stout platinum ring or in a funnel completely covered with paraffin. Pour through it 5–10 c.c. pure concentrated HF, collecting the liquid in the platinum dish containing the main part of the residue. Heat on a steam-bath for five minutes. Dilute with 25 c.c. cold water, decant the solution through the same filter, and wash the residue and the filter thoroughly. Then rinse the residue from the platinum dish into a casserole. Collect the solution in a second platinum dish. (Residue, P. 7; solution, P. 31).

Notes.

1. The HF dissolves silica and all the oxides of the niobium and tungsten groups, except that of tin, when this is present in large quantity; but this also dissolves on diluting the solution with cold water. All the substances specifically named in P. 5, N. 3 also pass into solution in HF, with the exceptions of ThF_4 and $\text{Th}_3(\text{PO}_4)_4$, of the Bi_2O_3 present in excess of about 6 m.grms., and of some $\text{Sn}_3(\text{PO}_4)_4$ when this is present in large quantity.

2. A residue undissolved by the HF may consist of one or more of the following substances, if the original substance was non-metallic:— PbSO_4 , BaSO_4 , SrSO_4 ; HgS , native MoS_2 ; MnO_2 , PbO_2 ; ignited or native Al_2O_3 , Cr_2O_3 , FeCr_2O_4 (chromite), SnO_2 , or TiO_2 ; AgCl , BiF_3 , ThF_4 , Prussian blue, $\text{Sn}_3(\text{PO}_4)_4$, $\text{Th}_3(\text{PO}_4)_4$

(as in monazite), certain silicates (such as cyanite, andalusite, tourmaline, beryl, zircon, topaz), S, C, SiC. It may consist of one of the following substances, if the original substance was a metal:—Au, Pt, Ir, Rh, Ru, or Os, or alloys of these, or certain alloys of iron (such as ferrochrome, ferrosilicon).

3. In spite of the rather numerous exceptions named in the preceding note, by far the larger proportion of substances ordinarily submitted to analysis, including almost all silicates, are decomposed by treatment according to the foregoing procedures.

Procedure 7.—Add to the residue insoluble in HF (P. 6) 15 c.c. HCl (1:20), and boil gently for five minutes. Then add slowly 10 c.c. water, keeping the liquid at its boiling-point. Decant while still hot through the filter previously used, if this contains any of the residue. [If it is doubtful whether the HCl has dissolved anything, evaporate the solution to dryness to determine it]. If the residue has been dissolved to a considerable extent, but not completely, boil it with successive portions of HCl (1:20) as long as a considerable quantity of substance is dissolved, diluting and decanting each time as before. To the residue add 3 c.c. HNO_3 (1:42), and 10 c.c. HCl (1:20), and heat on a water-bath for five minutes, or longer if an action is taking place. Dilute with an equal volume of water, filter through the same filter-paper, and wash the residue. Unite the HCl and aqua regia solutions. Separate the residue from the filter, or incinerate the latter if necessary. (Residue, P. 8; solution, P. 17).

Notes.

1. Of the substances named in P. 6, N. 2, which may constitute the undecomposed residue, it will be found that PbSO_4 , SrSO_4 , MnO_2 , and PbO_2 dissolve completely in 30 c.c. HCl (1:20) on five minutes' boiling, even when such quantity is present as contains 500 m.grms. of the metallic element, and they remain in solution on the addition of 20 c.c. boiling water. The same is true of fused AgCl up to a quantity containing 100 m.grms. Ag, of BaSO_4 up to 20 m.grms., and of $\text{Sn}_3(\text{PO}_4)_4$ in large quantity.

2. By the treatment with aqua regia, HgS , Au, and Pt (except when alloyed with another platinum metal) are also completely dissolved.

3. The cases in which a subsequent fusion must be resorted to are therefore rare. The important substances for which it is necessary are named in P. 8, N. 1 and 2.

Procedure 8.—If the residue insoluble in aqua regia (P. 7) is non-metallic and light coloured, and if it is thought to consist of a silicate or of BaSO_4 , or if there is no indication as to its nature, fuse it with Na_2CO_3 as directed in P. 9.

If the residue is non-metallic and light coloured, and if it is thought to consist of a metallic oxide, fluoride, or phosphate, fuse it with $\text{K}_2\text{S}_2\text{O}_7$ as directed in P. 12.

If the residue is metallic, or if it is non-metallic and dark coloured, fuse it with Na_2O_2 as described in P. 13.

Notes.

1. The important light coloured non-metallic substances which may occur in the residue insoluble in HF, HCl , and aqua regia are:— BaSO_4 , certain silicates, ThF_4 , native or ignited Al_2O_3 , TiO_2 , $\text{ZrO}_2\cdot\text{SiO}_2$, monazite, and SnO_2 . By fusion with Na_2CO_3 the silicates and BaSO_4 are readily converted into soluble compounds, but this method is ineffective with the other substances (except possibly ThF_4). All of these, except SnO_2 , dissolve in dilute H_2SO_4 after fusion with $\text{K}_2\text{S}_2\text{O}_7$. SnO_2 is best brought into solution by fusing it with twenty times its weight of a mixture of equal quantities of Na_2CO_3 and S in a porcelain crucible, extracting the mass with water, and treating the solution according to Part II., and the residue, after dissolving in hot HCl (1:12), and properly diluting by P. 71.

2. The important substances that may constitute a

dark coloured non-metallic residue are :—Chromite (FeCr_2O_4), graphite or coal (C), carborundum (SiC), molybdenite (MoS_2), and Prussian blue ($\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$). A metallic residue may consist of an alloy of iron (like ferrosilicon or ferrochrome), or of a platinum metal or alloy. Most of these substances require fusion with an oxidising flux, and all of them yield to it. The extremely powerful one, Na_2O_2 , is employed so that the method may be general; for even the platinum metals, if in a moderately fine state of division, are oxidised by it. A mixture of Na_2CO_3 and KNO_3 would effect decomposition of the other substances, and, if preferred, it may be substituted for Na_2O_2 , except when platinum metals are to be treated.

Procedure 9.—If its character makes fusion with Na_2CO_3 advisable (P. 8), mix the residue insoluble in aqua regia (P. 7) with ten times its weight of anhydrous Na_2CO_3 in a platinum crucible. Cover the crucible, and heat it for thirty minutes either over a powerful burner (preferably within a cylindrical porcelain jacket) or over a blast-lamp, adding more Na_2CO_3 if a perfectly fluid fusion does not result. Insert in the liquid mass a stout platinum-wire with a small horizontal ring at the lower end, and allow the mass to solidify completely. Then heat the crucible till the mass begins to melt around the sides, and remove it by means of the platinum-wire. Digest it on a steam-bath with 50 c.c. water till the mass is entirely disintegrated. Filter, and wash the residue. (Residue, P. 10; solution P. 11).

Notes.

1. If the mass is not removed from the crucible, its disintegration by the hot water is often very slow.

Procedure 10.—Heat the residue from the aqueous solution of the fused mass (P. 9) with 5 c.c. HCl (1·12) for five minutes, and add 25 c.c. hot water. Filter, and wash the residue. (Residue, P. 12; solution P. 71).

Notes.

1. Of the elements of the tungsten, niobium, selenium, and silver groups, tin and titanium are the only ones that are at all likely to be present in the HCl solution of the fusion of the residue (P. 7) insoluble in all the acids. As these elements are tested for also in connection with subsequent groups the solution is immediately precipitated with H_2S (P. 71).

Procedure 11.—Acidify the aqueous solution of the fused mass (P. 9) with HCl , evaporate the solution to dryness, and heat the residue in a hot closet at 120° for an hour. Heat the residue with 5 c.c. HCl (1·12). Add 25 c.c. water, filter, and wash the residue. (Residue, P. 6; solution P. 71).

Notes.

1. The solution of the fused mass is evaporated with HCl , and the residue heated at 120° and treated with HCl to separate silica, which is very likely to be present. A white insoluble residue probably consists of nothing but silica, but, if desired, this may be determined by warming it with HF (P. 6), and treating the solution by the subsequent procedures (P. 31).

2. Since it is very improbable that elements of the selenium and silver groups are present, owing to the fact that most, if not all, of their compounds are decomposed by the preceding treatment with various acids, the solution of the dehydrated residue is precipitated at once with H_2S .

Procedure 12.—If the character of the residue insoluble in aqua regia (P. 7) makes fusion with $\text{K}_2\text{S}_2\text{O}_7$ advisable (P. 8), or if this residue has been fused with Na_2CO_3 and undecomposed substance still remains on treating the fused mass with HCl (P. 10), pour the residue gradually into a platinum crucible containing ten times as much $\text{K}_2\text{S}_2\text{O}_7$ in a state of fusion. Cover the crucible, and keep the temperature at a dull red heat for twenty minutes. Cool the crucible, pour into it 2—4 c.c. H_2SO_4 (1·84) and heat

again, keeping the crucible covered until the whole mass becomes fluid. Cool the crucible, and gradually pour its (still liquid) contents into 30 c.c. water. Decant the solution from the residue, add to this 5—10 c.c. H_2SO_4 (1·20), and heat to boiling. Filter, and wash the residue. (Residue, P. 6, and if there is still a residue, treat it by P. 20). Unite the filtrate with the previously decanted solution. Add 2 drops HCl (1·12), shake the solution vigorously for five minutes with 1 c.c. moist precipitated Ag , and filter. (Precipitate, reject; filtrate, P. 71).

Notes.

1. The 2—4 c.c. H_2SO_4 are added at the end of the fusion to save the considerable time otherwise consumed in the disintegration of the mass by water, to dissolve as far as possible rare earth phosphates (as in monazite) which otherwise may separate in large quantity on the addition of water, and to hold titanium in solution, which it does even though the solution be boiled. Any undissolved residue is heated with H_2SO_4 (1·20) in order to dissolve these phosphates and also any double sulphates of the rare earths (like $2\text{K}_2\text{SO}_4 \cdot \text{Th}(\text{SO}_4)_2$) which may have been precipitated in crystalline form.

2. An insoluble residue may consist of SiO_2 , which is ascertained by treating it with HF (P. 6) and evaporating the solution to complete dryness after the addition of a little H_2SO_4 ; of alkaline earth sulphates, which are treated by P. 20, and of undecomposed substances (such as certain silicates, cassiterite, &c.), which would be left as a residue upon boiling with Na_2CO_3 (P. 20), and which should be fused with Na_2CO_3 (P. 9), or with a mixture of Na_2CO_3 and S (P. 8, N. 1).

3. The solution is first shaken with Ag to remove the platinum which is dissolved from the crucible by the acid flux; if this is not removed a precipitate will be obtained with H_2S even though no elements of that group are present. The Ag precipitate is rejected, since it cannot contain mercury (owing to its volatility at a red heat) or gold (owing to the metal being unattacked by $\text{K}_2\text{S}_2\text{O}_7$), and is very unlikely to contain palladium or platinum (aside from that taken up from the crucible), and since these are the only elements precipitable by silver from a solution containing little HCl (see Part IV.).

Procedure 13.—If its character makes fusion with Na_2O_2 advisable (P. 8), introduce the residue insoluble in aqua regia (P. 7), gradually if a violent action occurs, into a nickel crucible in which 5 grms. Na_2O_2 have been brought to a state of fusion. Heat the lower part of the crucible to dull redness, maintaining a temperature sufficient to keep the mass fluid for from five to twenty minutes, according to the readiness with which the residue is attacked. After cooling, place the crucible on its side in a covered casserole, add 50 c.c. cold water, and, after the violent effervescence has ceased, warm gently. Rinse out the crucible, transfer the solution and residue to a flask, and add gradually HCl (1·20) until the black residue of $\text{Ni}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$ dissolves, meanwhile keeping the solution cold. If complete solution does not result, decant the solution, after settling, from the residue, boil the latter with HCl (1·20), and unite the solution and any residue with the decanted solution. Transfer the mixture to a 200 c.c. distilling flask, having its side arm bent downwards and dipping into 10 c.c. 5 per cent NaOH solution in an Erlenmeyer flask surrounded by a large beaker of cold water. Close the flask with a cork through which passes a straight tube reaching to the bottom. Boil the solution for five to ten minutes, taking care that all the distillate condenses. Replace the NaOH solution containing the distillate by a fresh portion of NaOH solution, and distil again for five minutes. (Distillate, P. 14; residual solution, P. 15).

Notes.

1. Of the substances possibly present in a dark coloured or metallic residue, the platinum metals and their alloys are most difficultly attacked by Na_2O_2 . They should therefore be rather finely powdered, which is usually best

accomplished by pounding the substance in a diamond steel mortar. It is not necessary, however, to resort to the special methods of producing an extremely fine state of division, like fusion with lead, which have to be employed when other methods of attack, like heating with NaCl and Cl_2 , are to be used. Twenty minutes' fusion is sufficient with 500 m.grms. of the most resistant alloys.

2. As the nickel crucible is much attacked by the flux, the fusion should not be unduly prolonged. Silver and platinum crucibles are also strongly attacked, and have no advantage in this respect, while they have the disadvantage of being much more expensive.

3. The flux Na_2O_2 can now be obtained commercially in a fair degree of purity, being made from metallic sodium; it often contains some iron, however. Nevertheless, to determine the nature and approximate quantity of the impurities introduced from the crucible and flux into the solution to be analysed, a blank fusion and an analysis of the fused mass should be made.

4. Upon treatment of the fused mass with water, a violent evolution of oxygen occurs, and a large quantity of a fine black precipitate consisting of $\text{Ni}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$ separates. This dissolves completely on the addition of HCl .

5. The products resulting from the fusion of the substances (named in P. 8, N. 2) possibly present in the residue, and treatment of the fused mass with water, are as follows:—Chromite, Fe_2O_3 and Na_2CrO_4 ; carbon, Na_2CO_3 ; carborundum, Na_2CO_3 and Na_2SiO_3 ; molybdenite, Na_2MoO_4 and Na_2SO_4 ; Prussian blue, Fe_2O_3 and Na_2CO_3 ; ferrosilicon or ferrochrome, Fe_2O_3 and Na_2SiO_3 , or Na_2CrO_4 ; platinum, $x\text{Na}_2\text{O} \cdot \text{Pt}_2\text{O}_3$; iridium, $x\text{Na}_2\text{O} \cdot \text{IrO}_3$; rhodium, $\text{RhO}_x(?)$; osmium, $\text{Na}_2\text{OsO}_5(?)$; ruthenium, $\text{Na}_2\text{RuO}_5(?)$. All of these products, except Fe_2O_3 , $x\text{Na}_2\text{O} \cdot \text{Pt}_2\text{O}_3$, $x\text{Na}_2\text{O} \cdot \text{IrO}_3$, and RhO_x , dissolve upon treating the fused mass with water. Na_2CrO_4 imparts to the solution a pure yellow colour, Na_2OsO_5 a yellow-orange colour, and Na_2RuO_5 a dark orange-red colour. All of the products insoluble in water dissolve on the addition of HCl to the solution or on heating the residue with HCl (1:20), except a part of the $\text{Pt}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ when present in large quantity. The $\text{Pt}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ produced by action of the acid on $x\text{Na}_2\text{O} \cdot \text{Pt}_2\text{O}_3$ forms a dense yellow powder, which is dissolved only slowly by hot HCl (1:20), or even aqua regia. $x\text{Na}_2\text{O} \cdot \text{IrO}_3$ dissolves in HCl with production of a dark blue solution.

6. The solution must be kept cold during the neutralisation, since otherwise osmium may be lost in the form of the very volatile OsO_4 , which is formed when a Na_2OsO_5 solution is acidified. The solution must not be filtered through paper, as this immediately reduces Na_2RuO_5 with formation of a black deposit.

7. The OsO_4 (osmium tetroxide) set free when the Na_2O_2 solution is acidified distils over with great readiness (usually within two or three minutes), since in the pure state it boils not far from 100° , and since it dissolves in water apparently without change. The vapour has an odour somewhat similar to that of chlorine, and is extremely irritating to the eyes and nose. The distillate assumes a yellow colour when a little osmium, a dark orange colour when much osmium is present.

8. Although a similar volatile oxide of ruthenium (RuO_4) exists, it is not formed when the Na_2O_2 solution is heated with HCl ; on the contrary, the Na_2RuO_5 present is reduced with formation of RuCl_3 . Consequently no ruthenium distils over.

9. If osmium were present in the original substance in the form of one of its salts, it would be completely volatilised in the first treatment with HNO_3 (P. 1) or in the subsequent evaporation (P. 2 or 3); for all soluble osmium compounds yield OsO_4 when boiled with HNO_3 . Therefore, if its presence in such a form be thought possible, the first treatment of the substance with HNO_3 (1:20) should be carried out, as indicated in P. 1, in a distilling flask, the liquid boiled for two or three

minutes, and the distillate collected as in this procedure, and tested by P. 14. As osmium is in practice very rarely met with except in the metallic form, it is, as a general rule, unnecessary to complicate in this way the procedure for the preparation of the solution.

10. Since metallic osmium, both in the pure state and alloyed with iridium or other platinum metal, is scarcely attacked by aqua regia, unless it has been brought to an extremely fine state of division by a chemical method, there is little danger of completely dissolving and volatilising it in the treatment with that solvent in P. 7. Still, if it is desired to determine with certainty the presence or absence of a small quantity of osmium, it is best either to heat the residue undissolved by HNO_3 , HF , and HCl with the aqua regia in a distilling flask, and to collect and test the distillate as in P. 13 and 14, or to fuse the residue with Na_2O_2 (as in P. 13) without treating it with aqua regia at all.

Procedure 14.—Add to the distillate (P. 13) four or five drops 20 per cent $\text{Na}_2\text{S}_2\text{O}_3$ solution, acidify with HCl (1:12), keeping the liquid cool, and add to the solution one-fifth its volume of HCl (1:12). (Precipitate and solution, reject).

Note.

1. OsS_2 separates as a brownish black precipitate. The test is obtained when only 0.5 m.grm. Os is present in the solution submitted to distillation. It is the volatility of the osmium and its presence in the distillate that is especially characteristic—not the fact of its precipitating with $\text{Na}_2\text{S}_2\text{O}_3$; for if they could be present in the distillate, other elements—for example, ruthenium—would give a similar precipitate.

Procedure 15.—Evaporate the residual solution from the distillation (P. 13) to dryness, and heat the dry mass at 120° for an hour. Then heat it to boiling with 20 c.c. HCl (1:02). Filter, and wash the undissolved residue. (Residue, P. 16; solution, P. 71).

Note.

1. The solution is evaporated and the salt mass heated at 120° , so as to make insoluble the H_2SiO_3 and H_2WO_4 that may be present. PtO_3 may also be present in the residue undissolved by the HCl (1:02); see P. 13, N. 5.

Procedure 16.—Treat the residue (P. 15) just as described in P. 6. (Solution in HF , P. 31). Add any residue undissolved by HF to the HCl solution (P. 15), and treat the mixture by P. 71, allowing the cold solution saturated with H_2S to stand an hour or more before filtering.

Notes.

1. Of the elements of the tungsten and niobium groups, only tungsten and titanium are at all likely to be present in this HF solution; for tin and antimony, even if present in the fused residue, would dissolve on treating the dehydrated residue with HCl (P. 15), and niobium and tantalum are not met with at all in alloys nor in compounds insoluble in HF . Hence, the procedure given for those groups may be shortened in its application to this HF solution, by the omission of those operations which serve only to remove and detect the elements almost certainly absent; or this HF solution may be united with the first HF solution obtained when the original dehydrated residue was treated with HF (P. 6).

2. The residue insoluble in HF , if of a yellow colour, may consist of Pt_2O_3 . It is added to the solution about to be precipitated with H_2S , because the reagent converts the Pt_2O_3 into Pt_2S_3 , which dissolves when the H_2S precipitate is subsequently treated with aqua regia.

Procedure 17.—Evaporate the mixed HCl and aqua regia solutions of the residue insoluble in HNO_3 and HF (P. 7) just to dryness. Heat the residue to boiling with 10 c.c. HCl (1:02), cool, and after two to three minutes filter. Wash the undissolved residue thoroughly with as little HCl (1:02)

as possible, adding the washings to the filtrate. (Precipitate, P. 18; filtrate, P. 71).

Note.

1. The residue undissolved by the HCl (1:02) may consist of AgCl, PbCl₂, PbSO₄, BaSO₄, and SrSO₄, which, though soluble in hot concentrated HCl, are only slightly dissolved by a small quantity of cold HCl (1:02). The solution may contain the other substances named in P. 7, N. 1 and 2, especially lead, manganese, mercury, gold, and the platinum metals. It is therefore united with the main solution and submitted to the regular scheme of analysis, beginning with the H₂S precipitation (P. 71).

Procedure 18.—Pour repeatedly through the filter containing the residue insoluble in dilute HCl (P. 17) a 10–15 c.c. portion of cold NH₄OH (0:90). Filter and wash the residue with NH₄OH (0:96). (Residue, P. 19). Acidify the filtrate with HNO₃. (Precipitate and solution, reject).

Note.

1. The residue is treated with NH₄OH to extract any AgCl present. Cold NH₄OH is used, since PbSO₄ is somewhat soluble in hot NH₄OH. The filtrate is acidified to determine whether any silver is present. The AgCl dissolves in the NH₄OH, owing to the formation of a salt with a complex cation, Ag(NH₃)₂·Cl'.

Procedure 19.—Pour repeatedly through the filter containing the residue undissolved by the NH₄OH (P. 18) a 10–20 c.c. portion of hot 25 per cent NH₄C₂H₃O₂ solution to which 5 per cent NH₄OH have been added. Filter and wash the residue with the NH₄C₂H₃O₂ solution until it is free from lead. (Residue, P. 20). Acidify the filtrate with HC₂H₃O₂, and add a few drops of a 10 per cent K₂CrO₄ solution. (Precipitate and solution, reject).

Note.

1. The residue is treated with NH₄C₂H₃O₂ to extract any PbSO₄ or PbO₂·H₂ present. Even 500 m.grms. Pb as PbSO₄ dissolve in 15 c.c. boiling NH₄C₂H₃O₂ solution. BaSO₄ is not appreciably soluble. A small quantity of SrSO₄ dissolves, but this does not precipitate with K₂CrO₄ in the confirmatory test for lead. Even if all the SrSO₄ present in the residue passes into the NH₄OH solution there is no danger of failing to detect strontium as a constituent of the original substance; for SrSO₄ is so soluble in dilute HNO₃ (P. 5) and dilute HCl (P. 17) that a considerable quantity of it will be found in the main solution; thus, 10 c.c. of cold HCl (1:04) or of cold HNO₃ (1:032) saturated with SrSO₄ contain about 10 m.grms. Sr.

Procedure 20.—Unite the residue insoluble in NH₄C₂H₃O₂ solution (P. 19) with the residue from the K₂S₂O₇ fusion (P. 12) after its treatment with HF. Transfer these, with the filters if necessary, to a casserole, add 10 c.c. saturated Na₂CO₃ solution, and boil gently for ten minutes, replacing the water which evaporates. Dilute with an equal volume of water, and filter. (Filtrate, reject). Wash the residue thoroughly, and pour repeatedly through the filter containing it a 10 c.c. portion of hot HCl (1:02). (Solution, P. 71).

Notes.

1. Even 500 m.grms. Sr as SrSO₄ are completely converted to SrCO₃ by this procedure. An equal quantity of BaSO₄ would require boiling with two or three successive portions of Na₂CO₃ solution, but as the quantity of BaSO₄ that can be present in this residue cannot be very large, owing to its rather small solubility in HCl (1:20) (see P. 7, N. 1), a single boiling suffices.

2. The Mass Action Law requires that the difficultly soluble sulphate be transformed into carbonate until the ratio (C_{SO₄}/C_{CO₃}) of the concentrations of the SO₄ and CO₃ ions in the solution becomes equal to the ratio (SP_{MSO₄}/SP_{MCO₃}) of the solubility products of the sul-

phate and carbonate in pure water. Now since the second ratio, according to recent solubility determinations, has (at 18°) a value larger than 60 in the case of the two strontium salts, a very large amount of SrSO₄ would have to be transformed to Na₂SO₄ before the ratio C_{SO₄}/C_{CO₃} attained this value. On the other hand, in the case of the two barium salts, the second ratio has apparently the value 0:25 (since it is found that the conversion ceases when C_{SO₄}/C_{CO₃} = 0:25), so that after a certain amount of BaSO₄ has been transformed, the reaction ceases. Aside from this great difference in the equilibrium ratios, the rate of transformation is doubtless much less in the case of the BaSO₄, owing to its very slight solubility. It is to increase this that the solution is boiled.

(To be continued).

THE USEFUL PROPERTIES OF CLAYS.*

By ALLERTON S. CUSHMAN, Chemist, Division of Tests.

INTRODUCTION.

FROM the earliest dawn of history man has exercised himself in fashioning into products of beauty and utility the plastic materials which he found prepared for his hand on or under the surface of the earth. The stone age was followed by the bronze, and this in time by that of iron, and this in turn by the age of steam and electricity; but throughout all these changes the plastic arts have flourished in proportion to the height of civilisation that the peoples have reached. Science and art, poetry and history combine to lend fascination to a study of clays and clay working. Records of the manners and customs of old and almost forgotten civilisations, such as the Mycenaean, or the Mexican, are carefully gleaned by the archaeologist from the more or less crude linear markings and figures depicted on fragments of pottery and statuary which have come down to us. From the few rude earthenware chips which remain to tell us of our prehistoric ancestors to the finished and delicate porcelains of Dresden and Sèvres, the industry of man records its own development.

Although in the direction of pure utility, as in the manufacture of bricks, tiles, and common earthenware, much has been accomplished, the fact is before us that, in the production of works of art and beauty fashioned from clay, America is not to-day the equal of Europe. The reasons for this are various and need not be discussed here. It is sufficient to point out that they are not of such a nature as to prevent America from ultimately achieving the highest position of all in this domain. The fact that many tons of clay of various sorts are annually brought across the ocean to us for use in our potteries, might seem to indicate that our native clays were of themselves unfit for use. If indeed this were true, it would be an insuperable obstacle to final success, but the fact is that, although it may at present be more profitable to import a clay than to develop a native source, America undoubtedly possesses unusually rich clay and kaolin deposits, some of which are fitted for the production of the most delicate and beautiful objects. It is interesting to note that the pottery which has been a pioneer in works of art made entirely of native clays was founded and fostered by an American woman. It is by just such efforts that wider and further growth will come. In these days of ardent emulation and competition among the nations, it is fair to anticipate the time when an American name shall be added to those which stand for the highest achievement in ceramics, or the art of clay working. As soon as a greater number of individuals among our people become interested in the properties and possibilities of our native clay bodies, development is sure

* United States Department of Agriculture, Bureau of Chemistry, Circular No. 17.

to follow. Clay working is neither so difficult nor so expensive but that in some cases objects of art have been moulded in the home and burnt in private kilns. On the other hand, success is attained only at the price of diligent study and persistent effort. It is with the hope that the dissemination of knowledge concerning the useful properties of clay will lead to a wider popular interest in their study and use, that this article is written.

FORMATION OF CLAYS.

Clay may be defined as an earthy deposit, found on or below the surface, which when finely ground and mixed with water forms a mouldable or plastic mass and can be burned to a hard, stonelike substance after drying. The original crust of the earth was of course formed of the rocks which crystallised from a molten magma. These crystalline rocks of igneous origin underwent gradual crumbling and decay caused by the varied actions of the elements. It is probable that only students of rock structure realise how steadily and continually rocks are undergoing secondary changes and decay. "Enduring as the rocks" is an expression of merely relative truth. When rocks crumble the resulting material may be found either heaped up in places, in which case they are known as residual deposits, or the fine material may have been picked up in suspension by moving waters, sifted out and deposited at some remote place in beds or layers forming sedimentary deposits. These deposits once formed have been, in some cases, acted on by tremendous forces in the course of the great geologic periods. Folded and buried under great crumplings of the earth's crust they have been to varying degrees subjected to heat and pressure and have thus become metamorphosed. Consolidated into sedimentary rocks and shales they become again subject to decay. Changed and disintegrated, now acted on by percolating waters, in which it is known that many of these crystalline minerals are distinctly soluble, or again subjected to acid or alkaline solutions, as the case may be, it is little wonder that every useful earthy deposit found by man on the surface of the earth is to a certain degree unique in its properties, requiring special study and treatment in order to insure the highest degree of success in its working. Clays of nearly the same chemical composition and of similar physical texture, owing to some slight modification will yield entirely dissimilar results in mixing, moulding, and firing. Given in some particular locality a deposit which under certain treatment yields a definite and constant result to man's handicraft, it is doubtful whether, if the deposit becomes exhausted, exactly similar results could be produced elsewhere even by the selfsame artisans. It is to some extent owing to these reasons that the great potteries of the world maintain their distinctive styles, and also lose them as in the cases where the finest modern examples are inferior to the older work. The loss of the art of the ancients, renowned for their pottery and glazes, is possibly due to this cause more than to the inability of modern science and industry to duplicate their cunning in artifice. For the reasons outlined we find our clays with all shades of variation in their useful properties.

PRODUCTION AND IMPORTATION OF CLAYS.

The following figures taken from the statistics of the mineral resources of the United States, compiled by the U.S. Geological Survey for the year 1902, show in an interesting way the condition of our clay-producing industry:—Total imports of clays, 168,551 long tons, valuation 1,154,805 dols.; total domestic production of clays, 1,299,426 long tons, valuation 2,061,072 dols.

Altogether the total amount of clays imported into this country is between one-seventh and one-eighth of that produced here, while the valuation of the latter is less than twice that of the former. Doubtless in time the rich clay deposits of America will be developed to a point where this considerable importation of expensive clays will cease, and one of the factors in this progress will be a better understanding of the useful qualities of clays.

KINDS OF CLAY.

With few exceptions residual clays, or those derived from the decomposition of rocks in place, are fit only for the commoner grades of brick and earthenware. Nearly all the smoother and finer textured clays are formed from the sedimentary plastic products of rock decay. These beds may be, however, of a widely different nature, some being sandy, or to use a technical expression, "lean," and others very fine-grained, plastic, and "fat." By the accumulation of beds of fine-grained material, one on top of another, the clays become consolidated into shales. These shales, which are much used in certain localities, are sometimes as hard as rock, but when ground and mixed with water yield a plastic, workable mass. In actual pottery practice it is usual to mix several different kinds of clay, thus combining the useful qualities of each. Probably more than 90 per cent of all manufactured articles are moulded of a mixture of at least three clays.

The various sorts of clays have come to be distinguished by different names; thus one hears of stoneware, china, and brick clays; pipe clays, ball clays, fire clays, and kaolins. These distinctions are not very exact, and in most cases merely show the local use to which the clay is put. China clays are usually white or burn white, and when mixed with ball clay, ground feldspar, and quartz, are used in the manufacture of porcelain and other forms of white ware. Ball clay is the name given to very fat plastic clays which can be formed and moulded into shape and which will dry out to a mass of high binding power without suffering deformation. Used by themselves ball clays will rarely stand the fire well, but for mixing with good burning clays of low binding power and little or no plasticity they are very necessary. Florida supplies these clays to a considerable extent, but for special reasons they are at present very largely imported from England and Germany. Kaolins are made up of fine particles of the mineral kaolinite which results from the decomposition of feldspar. Kaolin, which, chemically speaking, is a silicate of aluminium, is supposed to be the essential ingredient in all clays, and it is not uncommon to read in various publications that kaolin furnishes the active clay base in all plastic clay. Recent researches made in the Division of Tests of the Bureau of Chemistry, however, show that such statements do not express the whole truth of the matter. Fire clays, as their name signifies, are those which do not fuse or melt except at very high temperatures, 3500° F. and over; although these clays are generally used in the manufacture of fire bricks, muffles, and linings for furnaces, they can be used for decorative purposes, as their very stability in the fire makes them easy to burn.

PHYSICAL PROPERTIES OF CLAY.

We may now turn to the consideration of the physical properties of clay, taking them in the following order; (1) Plasticity; (2) binding power (tensile strength); (3) slaking; (4) air shrinkage; (5) firing qualities—(a) fire shrinkage (distortion), (b) fusibility, (c) colour; (6) absorptiveness.

Plasticity.

It is a matter of common observation that the particles of all wet powders to a greater or a less degree cohere. If we take ordinary clean white sea-sand, grind it to an impalpable powder and mix it with a certain amount of water, we shall have a mass just sufficiently coherent to ball together. If, however, we try to mould the wet mass into a form it quickly crumbles and shows itself quite unworkable. From this extreme up to the most plastic of the ball clays which will respond to every touch of the artist's hand and preserve every line of the graver's tool, we find among the fine-grained materials on the earth's surface every grade of variation.

The cause of this wonderful property has been much discussed by students of clay structure. Investigations carried on in the Division of Tests show that the effect is due to the presence of a certain proportion of particles

which actually soften and become sticky under the action of water. It has been noted that purely crystalline particles do not make plastic masses, but there is another kind of matter than that which appears in a crystalline form. This is broadly defined as amorphous substance. Only one kind of amorphous matter, however, is active in producing plasticity. Glass is an amorphous, non-crystalline material, but powdered glass is no more plastic when wet than is sand. The particles which are active in forming coherent masses are highly hydrated, that is, they contain so-called water of combination, which disappears into some sort of porous structure too fine to be seen even under the most powerful microscope. Clays, even when thoroughly dried in the sun and air so that they have every appearance of being dry powders, will sometimes contain as much as 12 or 14 per cent of this combined water. If the clay is heated to a sufficiently high temperature to drive off this water all plasticity and clay likeness is gone. Thus brick dust is no more plastic than sand or glass-powder. The particles have not become crystalline by heating, but the active hydrated particles have been changed into dead amorphous ones. These active particles which become coherent when wet are called *colloid* (which means glue-like), to distinguish them from the inactive crystalline and amorphous grains which are also present in almost every clay.

Binding Power.

It is this property which provides strength in the air-dried clay so that articles fashioned of it can be transported to the kiln without crumbling and breaking. It is a very important quality and the purer clays and kaolins are often deficient in it. The property is tested in the laboratory by moulding briquettes of a special shape, which after drying out are pulled apart in a machine designed for the purpose. The strength of different kinds of clays, as determined in this manner, is given in the following table:—

Tensile Strength of Clays.

	Pounds per sq. inch.
Pure kaolins.	5—20
Common brick clays	30—100
Pottery clays	100—500
Ball clays and other very plastic clays	200—500

It is a curious fact that though high binding power is usually associated with high plasticity, this is not invariably the case. Some of the plastic clays of New Jersey in use in the potteries are of comparatively low binding power. This can be explained, however, by the colloid theory as outlined in the preceding paragraph better than by any other theory as yet advanced. There are various kinds of particles which assume to varying degrees the soft, almost viscous, condition which leads both to plasticity and binding power. In order to illustrate what is meant let us suppose that an inert, non-plastic powder were to be mixed with egg albumen on the one hand and with a glue solution of equal viscosity on the other. Masses of some plasticity would be obtained in both cases, but on drying out the binding power of the glue would be much higher than that of the albumin. The difference in such a case is attributable solely to the kind of cementing material which is present and its individual character. In addition to this it is undoubtedly true that the shape and size of the particles, and the proportional amount of plastic and non-plastic particles present have an important influence on these properties.

Slaking.

The slaking of clays refers to the quality possessed by some of them of rapidly disintegrating and falling to powder when lumps are thrown into water. Such clays are usually less dense; that is to say, bulk for bulk they are less heavy than those which do not possess this property. Clays that slake, if touched to the tongue will adhere to it, sometimes so strongly that it is painful to draw the tongue suddenly away. Both this effort and the slaking are caused by a vigorous indrawing of water into the porous structure

of the particles. In more dense clays this porous structure is already "stuffed" sometimes with water and quite often with other substances both of organic and inorganic origin. The truth of this is readily shown by a very simple experiment. Glycerin is not absorbed into the clay structure rapidly enough to produce slaking; if, therefore, a lump of slaking clay be soaked in glycerin over night it can be transferred to water, in which it will then be found to behave as does any non-slaking clay.

Clays that have been slaked and the powder moulded into masses and air dried do not again disintegrate when wet, as the porous structure is then sufficiently saturated with water to decrease the action. The power to slake readily is often a great advantage, as it enables hard clay masses from the bank to be disintegrated by weathering and thus does away with the necessity for elaborate grinding processes.

Air Shrinkage.

Air shrinkage is that which takes place during the air-drying of a clay mass and is caused by the evaporation of the water, both that which has been used in mixing and a portion of that which the clay contains. As has been explained, very plastic clays possess a greater number of the active hydrated particles with a porous structure, so that we should expect these clays to exhibit a higher shrinkage than lean clays, and this is actually found to be the case. Everyone is familiar with the way glue-like bodies shrink on drying. This shrinkage varies in different clays from 1 to as high as 10 per cent. We now begin to see why the skill of the potter is highly taxed even before his ware goes to the kiln. If he selects a clay which from its plasticity and binding power is all that could be desired, it is probable that its high air shrinkage will cause it to deform and check (crack) on drying out. Sometimes by very slow and careful drying the danger can be avoided, but usually another leaner material, sometimes even sand itself, is mixed in just such an amount as to reduce the shrinkage without too far lowering the other useful qualities.

Firing Qualities.

Many difficulties must be overcome in order to obtain a clay mixture which will burn well in the kiln and produce the desired result with the utmost economy. Of course the selection of the right kind of kiln and the proper control of the fire is of paramount importance. Such questions cannot be treated in an article of this nature and larger works on the subject must be consulted.

Fire shrinkage.—After a clay mass is thoroughly air-dried it undergoes a further shrinkage on heating as the water of combination already referred to is driven out, and the particles softened by incipient fusion followed by vitrification, draw together and adhere. By incipient fusion is meant the point at which the particles become soft in the fire and by vitrification the point at which they fuse together. Common bricks and earthenware are baked only to this first point and retain an open and porous structure, the bond of incipient fusion being sufficient to form the clay into tough, stone-like materials. Paving bricks and many kinds of stoneware are vitrified.

Fusibility.—It is well known that if pure crystalline substances are heated they become gradually hotter without apparent softening until a certain critical thermometric point is reached, at which the crystals suddenly melt and the mass assumes a liquid condition. If, on the other hand, a non-crystalline, amorphous substance like glass is heated, it begins very soon to soften and continues to grow continually more viscous until it finally flows. In other words, crystalline substances have sharp and definite melting points while amorphous substances have none at all, but soften gradually to the point of flow. As has already been mentioned, there is evidence to show that clays are mixtures of crystalline and amorphous particles in varying proportions, and it may now be further pointed out that, in the fire, clays behave just as we should expect such mixtures to do. If clays had a sharp melting point,

owing to the difficulty of exact control of temperature, the potter would be in continual danger of melting his ware to formless lumps, while on the other hand he could obtain no vitrified bond unless the particles first softened to the point of incipient fusion. As a matter of fact in most clays the point of incipient fusion is lower by from 100° to 500° F. than the point of vitrification, and this point in its turn may be many hundred degrees below the point of deformation and flow. Common brick clays will usually fuse at 2000° F., while many of the better grades of clays will stand 3000° without viscosity or deformation, while fire clays go as high as 3500° and even more. It will be apparent from what has been said that a clay which will stand a considerable increase in temperature above a given point without softening to the point of deformation and flow will be—other things equal—the safest and easiest clay to burn.

We have now to consider briefly the elements which actually determine the fusibility of clay. Quartz is an oxide of silicon formed by the association of two atoms of oxygen, with one atom of the element silicon to form the oxide silica, which is expressed by chemists by the symbol SiO_2 . Silicon is one of a group of elements which always form acid oxides, so called because if heated with the proper amount of certain alkaline or basic oxides like lime, which is an oxide of calcium (CaO), they will combine to form fusible slags which are neutral, showing neither an acid nor an alkaline character. Silica has a very high melting point, and lime an even higher one, so high in fact that it withstands the extreme temperatures of the electric arc. If, however, the two oxides be mixed together the fusing point is lowered. Thus in clays the point of fusion depends upon the amount of fluxing agents present, such as the basic substances, iron oxide, soda, potash, lime, and magnesia; and, although fineness of grain is also an element in determining fusibility, the point of fusion will usually fall with the percentage of these basic substances present. For this reason the common red brick clays which get their colour from iron oxide are, as a rule, of low fusing point.

Colour.—The colour of a clay before it is burned is of little importance except in so far as it serves to indicate the presence of iron. In the kiln, however, except in perfectly white clays which burn white, colour changes invariably take place. Many black clays stained by organic matter burn white, while others burn to reds, buffs, and cream colours. Nothing of importance has ever been accomplished technically in causing a dark burning clay to burn white. It is known that an increase in the amount of lime will produce a paler burn if the colour is due to iron, but, on the other hand, such an admixture has certain deleterious effects, such as lowering the fusing point unequally.

Absorptiveness.

The power that some clays have to rapidly absorb water and other substances has already been discussed. This property is frequently made use of in the arts. In addition to this action certain unctuous varieties of clay which will not usually adhere to the tongue have the power of removing colouring matters from solutions by actually adhering to the fine particles of matter held in suspension and "sweeping" them away. These clays are known as fullers earth and are much used as clarifying and bleaching agents. They are usually of a greyish-green colour, very soft and greasy to the touch, and if placed on the tongue they appear to melt away.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton Browne, M.D., F.R.S., Treasurer and Vice-President in the Chair. Messrs. W. A. Adam, W. A. Harper, J. B. Lightfoot, G. A. Moore, M. H. K. Poser, and Professor J. Perry, F.R.S., were elected Members.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 15th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

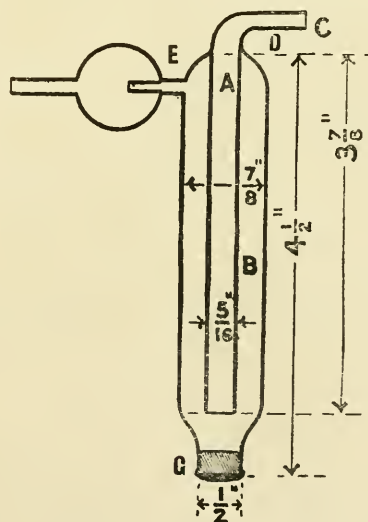
(Concluded from p. 152).

63. "*Aromatic Sulphonium Bases.*" By SAMUEL SMILES and ROBERT LE ROSSIGNOL.

It was shown that the action of thionyl chloride on phenetole in presence of aluminium chloride gives rise to *p*-phenetylsulphoxide and triphenetylsulphonium chloride; the latter is produced by the action of excess of phenetole on the sulphoxide. This reaction has led to the discovery of two other methods of preparing these aromatic sulphonium bases:—(1) From a sulphoxide and phenetole with a dehydrating agent; (2) from a sulphinic acid and phenetole with strong sulphuric acid. It is also shown that in this reaction a sulphoxide is formed as an intermediate product.

64. "*A New Form of Calcium Chloride Tube for Combustion.*" By ARTHUR EDWIN HILL.

The calcium chloride tube indicated in section in the accompanying figure consists essentially of an inner exit tube, A, which is enclosed within a larger inlet tube, B, the latter being fused to the tube A at D, and carrying a side-tube, E, provided with the usual form of bulb in which water can collect as liquid. The apparatus is easily filled by inverting it and pouring finely granulated calcium chloride into both the tubes A and B; before filling, a little glass-wool should be inserted at the top of both the inner and outer tubes, and after charging with calcium chloride more glass-wool is introduced; a suitable cork is then inserted at G; finally, this cork is cut off flush with the bottom of the tube and neatly covered with sealing-wax.



The bulk of the water produced in the combustion is condensed in the bulb on the tube E, the remainder being absorbed during the passage of the moist gases down B and up A. A double scrubbing action is thus obtained by the aid of a comparatively small weight of calcium chloride; this, in fact, in addition to its compactness, is a special feature of the tube and the cause of its efficiency. A certain amount of free space, not packed with the chloride, in the tube B, immediately above the point of connection

current to half value. The theory put forward to account for the phenomenon depended on the transportation of moisture over the surface by the current. In this way the effective thickness of the layer might be much diminished by a banking up of the moisture along the edge of one of the metallic electrodes.

Mr. ROLLO APPLEYARD expressed his interest in the paper, and pointed out that there were many ways in which electricity could pass between the electrodes. For instance, there was moisture leakage, surface leakage, the electrification effect, and the coherer effect. He suggested that experiments should be made so as to localise the separate effects.

Mr. A. CAMPBELL suggested that experiments might be made with electrodes of silver or platinum deposited electrolytically upon the glass so as to do away with the shellac used to stick down the tin-foil electrodes. He pointed out that moisture had a solvent action upon the glass, and that the film was not one of pure water, but of a solution of salts. He suggested that experiments might be made with films on ebonite or mica.

Mr. W. DUDELL asked if the effects described might not be due to the formation of a film of insulating oxide along the edge of one of the electrodes. He asked the author what time elapsed between a reversal and the first reading taken after it.

The CHAIRMAN, referring to the author's theory, said that the increase in conductivity on reversal of current was so sudden that he doubted whether the film would have time to spread. Also Mr. Duddell's film would, he thought, not disperse quickly enough.

Prof. TROUTON, referring to the separation of effects, said he had desiccated the glass plates and found them insulators. There was, therefore, no conductivity through the glass. He had used platinum melted on to glass, and got the same effects, so that they could not be due to the shellac used in pasting down the tin-foil. Replying to Mr. Duddell, he said that the time elapsing between a reversal and the first subsequent reading was of the order of a tenth of a second.

A paper on "*The Construction and Use of Oscillation Valves for Rectifying High Frequency Electric Currents*," was read by Prof. J. A. FLEMING.

The author recalled the fact that as far back as 1890, when investigating the Edison effect in glow-lamps, he had shown that the space between the incandescent carbon filament and an insulated metal plate placed in the vacuum bulb possessed a unilateral conductivity, negative electricity being able to pass from the filament to the plate, but not in the opposite direction. This led him to suggest an arrangement of the above kind for separating out or rectifying the oppositely directed currents in an alternating current. This effect was now recognised as due to the copious emission of negative ions or electrons from the incandescent carbon. It was by no means obvious, however, before trial, that any such rectifying arrangement or valve would operate with currents of very high frequency. For example, electrolytic rectifiers such as the aluminium-carbon cell were not available for high frequency currents because a time element entered into the chemical actions involved. In 1904, however, the author discovered that if the carbon filament in an electric glow-lamp was surrounded with a metal cylinder connected to an insulated terminal by a wire sealed through the bulb, and if the filament was made incandescent by an insulated battery, then between the insulated terminal and the negative pole of the battery a unilateral conductivity existed which was operative with currents of any frequency, and the valve so made might be employed to render electrical oscillations measurable by an ordinary sensitive galvanometer. The author exhibited oscillation valves made on this plan, and also showed their uses. If placed in series with a galvanometer, in the circuit of a coil of wire acted upon inductively at a distance by oscillations created in another circuit, the valve gives instructive information as to the damping in the primary

circuit. Thus he showed that when using a carbon-point spark-discharger in the primary oscillation circuit, much larger galvanometer deflections were obtained with very short sparks than with long ones. The author explained that the greatly lessened damping in the short spark caused the mean value of the secondary current to be increased, although the charge put into the primary condenser was diminished. The advantages of using multiple spark-gaps in oscillation circuits was also proved by the use of the valve. The author exhibited a multiple spark-gap discharger made with carbon rods, and claimed for it a much greater constancy of action than a discharger made with metal balls. Experiments were also shown illustrating the manner in which the valve is of use in showing the shielding action of thin metal sheets placed between primary and secondary oscillation circuits. Dr. Fleming also exhibited an experiment showing the copious emission of negative ions from the glower of a Nerst lamp at atmospheric pressure. A Nerst oxide glower was placed horizontally near a brass tube filled with water to keep it cool, and on glowing the oxide rod with a continuous current, it was shown that the space between the hot rod and the cool tube possessed a unilateral conductivity, and would only pass negative electricity in one direction. The author referred to the employment of carbon-filament oscillation-valves such as he had described as wave detectors or cymoscopes in connection with wireless telegraphy. Finally, it was pointed out how, by the use of an electrodynamicometer and galvanometer in series, the amount of rectification produced by the valve could be measured, and it was shown that it might amount to 89 or 90 per cent.

Dr. R. T. GLAZEBROOK expressed his interest in the paper, and hoped that Dr. Fleming would be able in a further communication to give numerical data so that the sensitiveness of the arrangement described could be compared with those of other rectifying devices.

A paper on "*The Use of the Cymometer for the Determination of Resonance Curves*," was read by Mr. G. B. DYKE.

The experiments described in the paper were made with a view to the adaptation of the direct-reading cymometer to the delineation of resonance curves and the determination of the logarithmic decrements of wave trains and the resistance of oscillating sparks. A special form of ammeter was inserted in the cymometer circuit, enabling the current to be observed for any position of the instrument. The ammeter used was of the hot-wire type, with a bismuth-iron junction in contact with the hot wire, the E.M.F. of the junction—and hence the current through the fine wire—being read off from the deflections of a single pivot galvanometer of low resistance. The results of the work of Bjerknes and Drude on the oscillation transformer are referred to, and the application of their final equations to the determination of logarithmic decrements from the resonance curve discussed. Precautions to be taken in the determination of resonance curves in practice are enumerated, and an example is given of the calculations involved in the determination of the logarithmic decrement and the resistance of an oscillatory spark. The double frequency set up in closely coupled oscillation circuits is shown by means of the resonance curve of a wireless telegraph aerial, the mathematical deductions of Oberbeck being thereby confirmed.

Mr. A. CAMPBELL asked the author if he could give an idea of the sensitivity of the hot-wire ammeter. He pointed out that if the instrument was used in a vacuum, the sensitivity was much increased.

Mr. W. DUDELL said he had tried thermo-junctions in a vacuum and found their sensitivity increased five or ten times. He suggested that the author should replace the bismuth in the junction by constantan.

Mr. DYKE, in reply to Mr. Campbell, said that a current with a maximum value of 0.17 ampère gave a deflection of 80 divisions.

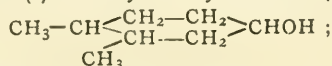
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

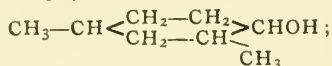
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 10, March 5, 1906.

Sub-oxides of Carbon.—M. Berthelot.—A new volatile suboxide of carbon, having a composition intermediate between CO and CO₂, and of formula C₃O₂, was discovered and isolated by Otto Diets and Bertram Wolf quite recently. It is a liquid boiling at +7°, which spontaneously decomposes. The authors prepare it by the action of phosphoric anhydride on malonic ether, C₃H₄O₄—2H₂O = C₃O₂. The present author observes that it is not correct to attribute the name suboxide of carbon solely to this body, as it represents a whole family of bodies and not a single specimen. He has, in fact, prepared a number of these sub-oxides, and predicts the speedy preparation of many others.

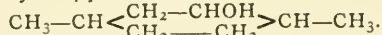
Synthesis of Three Secondary Dimethylcyclohexanols.—Paul Sabatier and A. Mailhe.—The direct hydrogenation of the xlenols allows of the isolation of three secondary dimethylcyclohexanols out of the six possible by theory. Two others had previously been prepared by other methods. The points of ebullition of these three secondary alcohols are 189°, 179°, 178·5°, and are notably higher than those of their tertiary isomers, which are 166°, 169°, and 170°. The composition of the compounds is:—(1) Dimethyl-1. 2-cyclohexanol-4,—



(2) dimethyl-1. 3-cyclohexanol-4,—



(3) dimethyl-1. 4-phenol-2,—



Selenious Anhydride.—Æhsner de Coninck.—The author determines the densities of different aqueous solutions of SeO₂. He then investigates the reactions of SeO₂ with HNO₃, H₂SO₄, PCl₅, PCl₃, hydrazine, and hydroxylamine.

Calcium and Strontium Iodomercurates.—A. Duboin.—Already noticed.

Nature of the Decomposition of an Aqueous Solution of Copper Sulphate by certain Aluminium Alloys.—H. Pécheux.—The author investigates the theory of the nature of the decomposition of an aqueous solution of copper sulphate with a small piece of bismuth-aluminium alloy, and proves that the reaction takes place in the following three stages:—

1. $2\text{Al} + 6\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2 + \text{H}_6.$
2. $\text{H}_2 + \text{SO}_4\text{Cu} = \text{SO}_4\text{H}_2 + \text{Cu}.$
3. $3(\text{SO}_4\text{Cu}) + 2\text{Bi} = (\text{SO}_4)_3\text{Bi}_2 + 3\text{Cu}.$

Estimation of Cadmium.—H. Baubigny.—The author proposes to estimate cadmium by the following processes:—
1. Filtration of the precipitate into a weighed funnel of tubular form containing a plug of flax, washing free from acid and calcining in such a manner as to destroy the last trace of organic matter in order to eliminate any chance of loss of cadmium due to reduction. 2. Desiccation of the sulphide in a current of hot air. 3. Treatment by sulphuretted hydrogen gas at a red heat by passing a current of this gas through the filter-tube. 4. Elimination of free sulphur by a current of hot air. 5. Weighing.

Thermo-chemistry of the Hydrazones and the Osazones of α-Diketones and Reducing Sugars.—Ph. Landrieu.—The heats of combustion of a series of

hydrazones and osazones corresponding to the α-diketones and reducing sugars have been determined by means of the calorimetric bomb. The heats of combustion can be used to calculate the quantities of heat which correspond to the fixation of one or two molecules of phenylhydrazine on to the diketones and the sugars.

Benzidine-aniline, Diphenylbidiazoaminobenzene, and Diphenyldisazoaminobenzene.—Leo Vignon.—Benzidine and aniline can be made to unite by two methods—tetrazobenzidine reacting on aniline, or the reaction of diazobenzene on benzidine. An investigation of these reactions, and the formation of diphenylbidiazoaminobenzene, gives an interesting example of the diazoic group in the two reactions.

Antimony Tartrate.—J. Bougault.—The use of alcohol should be avoided in the preparation of antimony tartrate. By replacing the alcohol with acetone, a well-defined product is obtained, crystalline and having the formula C₄H₃SbO₆; that is to say, antimony tartrate, C₄H₅SbO₇, less one molecule of water. It is doubtful whether the compound C₄H₅SbO₇ has been obtained in a pure state. Probably all the substances to which this formula is attributed, having been prepared by means of alcohol, ought to contain products of etherification mixed, doubtless, with the compound described in this paper. The differences between M. Guntz's results and those of M. Berthelot on the subject of the heat of solution of Sb₂O₃ in tartaric acid can possibly be explained by the new facts quoted in this paper without employing the hypothesis of two isomeric tartrates, of which latter hypothesis, however, the author does not deny the possibility.

MEETINGS FOR THE WEEK.

TUESDAY, 10th.—Faraday Society, 8. "The Rotating Electric Steel Furnace in the Artillery Construction Works, Turin," by Ernesto Stassano. "Electrothermics of Iron and Steel," by Ch. A. Keller. "Recent Developments in the Gin Electric Steel Furnace," by Gustave Gin. "The Cleaning of Work by means of the Electric Current," by H. S. Coleman.

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THE CHEMICAL NEWS.

VOL. XCIII., No. 2420.

NOTES ON THE CLEANING OF WORK BY MEANS OF THE ELECTRIC CURRENT.*

By H. S. COLEMAN.

UNDER certain conditions, work, consisting of iron and brass articles to be nickel-plated, may be cleaned by means of the electric current. Having large quantities to deal with, I could not get sufficient scoured by hand to keep the plating vats fully loaded. After increasing the staff of operators and getting little better results; I was advised to try cleaning by means of the electric current. Cables were carried to the iron tank containing a boiling solution of potassium hydrate (brown Montreal potashes), sp. gr. 1.2° T. A series of experiments were performed, chief of which are given below.

Experiment 1.—Using the iron tank as the cathode, and the work to be cleaned as the anode.

Current flowing for five minutes.

P.D. 1.75 volts.

Result.—Part of the grease appeared to be removed, but the surface of the work (cathode) was covered with a brown-stained deposit, which could not be removed by acid or cyanide dip.

Experiment 2.—Using the iron tank as the anode, and the work the cathode.

Current flowing for five minutes.

P.D. 1.5 volts.

Result.—The work was free from grease and dirt, but the surface was covered with a lead-coloured stain or deposit, which could not be removed by acid dips, and only very slowly by a cyanide dip.

At this stage it was decided to try the effect of reversing the current, in order to remove this "stain" or "deposit," if possible.

Repeating Experiment 2, I waited until the "stain" appeared, and then reversed the current. The result was very satisfactory; the "stain" disappeared, and the surface of the work became clear and bright.

A final experiment was performed to determine the current density required for successful working. This was as follows:—

Approximate area of work	..	8½ sq. ft.
Current		68 amperes.
Working C.D.		8 amperes per sq. ft.
P.D.		2½ volts.

In Experiment 1 the cathode (iron tank) did not show any signs of electrolytic action having taken place. In Experiment 2, however, the anode (iron tank) was attacked, the surface being covered with a thin layer of oxide. This I anticipated from the fact that, during the time the work is the cathode the whole of the grease and dirt is removed, the reversal to anode being only necessary for the removal of the stain.

That the cleaning is due to an electrolytic, and not merely a chemical change, I feel convinced, for unlike ordinary chemical potash cleaning, the same result is obtained by using a cold bath. The cleaning, however, is very much slower than with the hot bath. Electrolysis takes place, and minute quantities of metallic sodium (using sodium hydrate solution only) appear around the cathodes (work), and occasionally take fire. In actual working it is much better to use the hot solution.

By this process the grease, which consists chiefly of tallow, is saponified and remains in solution. The lighter

dirt is thrown upon the surface of the bath and may be skimmed off, the remainder consisting of very fine emery, falling to the bottom of the tank.

A working plant capable of cleaning a considerable quantity of work per day consists of the following, the necessary current being supplied from the plating dynamo:—

There is a wrought iron tank containing the cleaning solution. Over each end is erected a wooden structure, clear of the tank, to support the rods on which the work hangs. Along the top of each support is a flat copper strip, which is connected to the cable by means of a stud. The rods are made of H.C. hard-drawn copper. These make surface contact only, owing to the variety of articles to be cleaned. There is a resistance board and change over switch in the circuit.

In the first stage of the process the iron tank is used as the anode, and the work the cathode. A voltmeter is connected across the terminals of the bath for recording the difference of pressure, the current being recorded on the ammeter placed in the main circuit from the dynamo. The cleaning bath is made up of equal quantities of brown Montreal potash and sodium hydrate dissolved in water and kept boiling, sp. gr. 1.8° T.

The work, after wiring up in the usual way, is distributed along the copper rods in small bunches. The current is now switched on and adjusted until a difference of pressure of 2½ volts is recorded on the voltmeter. Immediately the surface of the work begins to change colour, which takes from 5 to 10 minutes; the current is then reversed for a short time, usually 30 to 40 seconds, until the surface is clear and bright. It is then switched off, and if the work is still dirty the operation is repeated. It is then thoroughly swilled in clean cold water, passed through suitable dipping solutions, electro-coppered, passed through clean, cold water again, and transferred to the plating bath.

The advantages of this process are:—

1. The work is cleaned in one-third of the time occupied by the older method of scouring by hand.
2. It is all wired up ready for plating, and the surface is not touched again by the hand until it is unwired after plating. This not only prevents a certain amount of stripping, but also saves the considerable time which would be occupied in wiring up again, after scouring by hand.
3. The work is rendered *chemically* clean, due to the action of the current working out all grease and dirt from parts where it is impossible to scour with a brush.
4. Time is saved in filling the vats, thus giving an increased output.
5. Saving of labour and materials.

THE USEFUL PROPERTIES OF CLAYS.*

By ALLERTON S. CUSHMAN, Chemist, Division of Tests.

(Concluded from p. 163).

PURIFICATION AND TREATMENT OF CLAYS.

IN ordinary brickmaking the clays are not usually given much preliminary treatment, as it would increase the cost of manufacture too much. In the manufacture of high-grade and art pottery, however, it is often worth while to go to any length in the effort to obtain an even standard of excellence. By means of grinding, washing, and sifting, the clays are reduced to the even and uniform texture which is absolutely essential to the production of high-class work. In addition to these processes it has been found that by allowing the clay masses which have been worked up with water to the consistency of a pasty dough to remain quietly in this condition for long periods, months or more, the binding power and plasticity increase. This

* A Paper read before the Faraday Society, April 10, 1906.

* United States Department of Agriculture, Bureau of Chemistry, Circular No. 17.

is called tempering or ripening the clay, and has been ascribed by some observers to bacterial action. It will readily be seen, however, that according to the colloid theory, as already outlined, the effect gained is caused by the gradual softening of the active particles under the influence of water.

A number of researches have been carried on during the last few years in an attempt to find cheap and economical methods for increasing the useful properties of clays. One experimenter, having occasion in 1901 to seek a clay of the highest possible binding power, soon learned that the material suited to his purpose could only be obtained in Europe, and more particularly in Germany. This experimenter immediately began to seek for a method of treatment for local clays which would develop the useful qualities necessary for his purpose. After some experimentation it was found that by a preliminary soaking in a 2 per cent solution of tannic acid, or the ordinary catechu of commerce, the binding power and plasticity of most clays were very much increased, while the air shrinkage was diminished. Even infusions of dried leaves and straw were found to produce the effect to some extent. The process was called the "Egyptianising of clay," on the somewhat fanciful theory that the ancient Egyptians used straw in brickmaking more on account of the strength given by the infusion than by the fibre.

This subject was investigated in a general way in the Division of Tests, and it was found that many substances have the effect of producing increased binding power and apparently increased plasticity in some clays. This is shown by the tensile strength tests given in the following table, made on a buff-baking brick clay. Each result is the average of 30 to 40 briquettes, from 10 to 12 having been made by each of three operators:—

Average Tensile Strengths of Treated Clays.

	Pounds per square inch.
Water	65
Two per cent solutions of—	
Tannic acid	153
Dilute ammonia	147
Alum solution	98
Iron alum solution	118
Dilute hydrochloric acid	63
Dilute caustic alkali (KOH)	80

Many other substances were also tried, but as the effects were not in all cases decisive they have not been included here. It will be observed that among the solutions tried, tannic acid, ammonia, and the alums were the most active in increasing the tensile strength.

On first thought these results are by no means easy to interpret. Tannic acid and the alums are astringent and of decidedly acid reaction in their water solutions, whereas ammonia is decidedly alkaline in reaction and detergent in its action. On the other hand, if alum is added to clay suspended in water to form a "slip," it will have a flocculating or coagulating effect upon the colloid particles, causing them to settle rapidly. Tannic acid and ammonia appear, in most cases, to have a deflocculating effect, and some clays, suspended in dilute ammonia, show no indication of settling after the lapse of several months. It is known that the colloid structure of clays is selective in its action: that is to say, tannic acid and ammonia will be taken out of solution and retained in the porous particles of a clay. This absorption then probably affects to some extent the flotation of the particles. In the writer's opinion the action of reagents in increasing the binding power of clays is twofold: (1) Deflocculation produces a better distribution of the colloid particles or a so-called "puddling" of the clay; (2) the colloids present are modified and developed, if not actually formed, by the reactions which take place. A further discussion of this interesting subject is of too technical a nature to be given here, but the question will be more fully treated in other publications.

USE OF CLAYS.

The various uses of clays is shown by the following list originally compiled for Mineral Resources, United States, 1891, published by the U.S. Geological Survey ("Clays of the United States East of the Mississippi River," by Heinrich Ries, U.S. Geol. Sur. Professional Paper, No. 11.)

Domestic.—Porcelain, white earthenware, stoneware, yellow ware, and Rockingham ware for table service and cooking; majolica stoves; polishing brick, bath brick, fire kindlers.

Structural.—Brick, common, front, pressed, ornamental, hollow, glazed, adobe, terra cotta; roofing tile; glazed and encaustic tile; drain tile; paving brick; chimney flues; chimney pots; doorknobs; fireproofing; terra cotta lumber; copings; fence posts.

Hygienic.—Urinals, closet bowls, sinks, washtubs, bath tubs, pitchers, sewer pipe, ventilating flues, foundation blocks, vitrified bricks.

Decorative.—Ornamental pottery, terra cotta, majolica, garden furniture, tombstones.

Minor Uses.—Food adulterant; paint fillers; paper filling; electric insulators; pumps; fulling cloth; scouring soap; packing for horses' feet; chemical apparatus; condensing worms; ink bottles; ultramarine manufacture; emery wheels; playing marbles; battery cups; pins, stilt, and spurs for potter's use; shuttle eyes and thread guides; smoking pipes; umbrella stands; pedestals; filter tubes; caster wheels; pump wheels.

Refractory Wares.—Crucibles and other assaying apparatus; gas retorts; fire bricks; glass pots; blocks for tank furnaces; saggars; stove and furnace bricks; blocks for fire boxes; tuyeres; cupola bricks.

Engineering Works.—Puddle; Portland cement; railroad ballast; water conduits; turbine wheels.

THE TESTING AND EXAMINATION OF CLAYS.

Although the testing of clays does not properly fall within the scope of a paper of this nature, a few words on the subject will probably be of interest. There is a very widespread impression that the nature and uses of a clay body will be revealed by a chemical analysis alone. It is true that combined with other data the results of complete chemical analysis are always of value, but the fact remains that clays of widely different properties will have almost identical chemical composition and *vice versa*. This is illustrated by the analysis of two samples, one a fat ball clay from Florida, and the other a rather lean fire clay from Kentucky.

Chemical Analyses of Two Clays.

Constituents.	Florida ball clay.	Kentucky fire clay
	Per cent.	Per cent.
Silica	47.01	47.70
Alumina	38.50	38.47
Iron oxide	0.35	Trace
Lime	0.08	0.112
Magnesia	0.15	0.11
Potash	0.83	0.57
Soda		
Combined water	13.78	13.03

In addition to the usual chemical analysis, it is customary to examine clays by methods of so-called *rational* analysis, in which the effort is made to distinguish between the silica which is combined with alumina as clay substance and that which is free as quartz or sand. While somewhat inaccurate such analyses are of undoubted value.

The amount of water required to be mixed with air-dried clays to bring them to just the proper consistency for moulding into forms varies greatly in different clays. It is evident from what has been said in an earlier paragraph that the smaller the amount of water present the less the danger from air shrinkage and the greater the economy of working, especially when artificial heat is used in the drying process. In a thorough report on the useful quali-

ties of a clay this property should always be tested. The physical characteristics which it is necessary to test in a complete examination of clay are best shown by the following laboratory form :—

Physical Characteristics of Clays.

	No. 722 (brick clay).	No. 925 (surface clay).	No. 926 (blue clay).	No. 930 (fire clay).
Water required (per cent) ..	17.4	28.0	19.0	18.5
Tensile strength—				
Average	65	35	130	110
Maximum	72	40	145	115
Air shrinkage (per cent) ..	2	3	7	3
Fire shrinkage (per cent) ..	2	—	8	2
Temp. (°C.) required for—				
Incipient fusion	1140	1000	1140	2500
Vitrification	1430	—	1430	—
Viscosity	1600	—	1600	—
Colour when burned	Buff	—	Coffee	Cream- whites

* Melted at 1400° to a slag.

When a sample of clay is sent to the laboratory to be tested the following rules should be observed by the shipper. The sample should not weigh less than 30 pounds in its air-dry condition, and it should represent as nearly as possible the average quality of the deposit from which it is taken. The laboratory should be put in full possession of such information as is available both as to the extent of the deposit and the purpose for which the report is desired. In some cases it happens that the interest in a clay is centered in its ability to hold water, for use in building canals or irrigation ditches. Clays vary as much in their permeability as in other qualities, but it is manifestly a waste of the chemist's time to investigate the firing qualities of a clay when simple percolation tests are all that is necessary.

THIRTEENTH ANNUAL REPORT
OF THE COMMITTEE ON ATOMIC WEIGHTS.
DETERMINATIONS PUBLISHED IN 1905.*

By F. W. CLARKE.

THE year 1905 has been remarkably prolific in determinations of atomic weight, and much of the work done was of unusually high quality. Some of the published researches deal with revisions of the more fundamental values, such as the atomic weights of nitrogen, chlorine, iodine, sodium, and potassium. These investigations have made it clear that a general revision and re-calculation of all the atomic weights is now needed, and the developments of the next year or two are likely to bring about many changes in the accepted table. Meanwhile, the International Committee (see Report in CHEMICAL NEWS, xciii., p. 54) advocates a conservative policy, and recommends that changes be deferred until important work now known to be in progress shall have been completed. Then the table of atomic weights, as presented in their report, can be revised intelligently, whereas such a revision undertaken now would be premature. The determinations published during 1905 are given in the following pages.

Nitrogen.

Guye (*Comptes Rendus*, cxl., 1241), from the density and critical constants of nitrous oxide, finds $N = 14.006$. Jaquero and Scheuer (*Comptes Rendus*, cxl., 1384) from densities and compressibilities of several gases, have determined the following molecular and atomic weights :—

$$H = 1.0078.$$

$$NO = 30.005, \text{ whence } N = 14.005.$$

$$NH_3 = 17.014, \text{ whence } N = 13.991.$$

Jaquero and Perrot (*Comptes Rendus*, cxl., 1542), from the density of nitrogen at 1067°, find $N = 14.008$. Guye

* From the *Journal of the American Chemical Society*, xxviii., No. 3.

and Pintza (*Comptes Rendus*, cxli., 51) determined the normal weight per litre of ammonia, nitrous oxide, and carbon dioxide (see under "Carbon," later). The figures for NH_3 and N_2O are as follows :—

NH_3 .	N_2O .
0.77080	1.97762
0.77069	1.97707
0.77073	1.97760
0.77099	
0.77076	

From nitrous oxide, compared with carbon dioxide in corresponding states, $N = 14.006$; from the critical constants, $N = 14.008$. Lord Rayleigh (*Phil. Trans.*, cciv., 369; *Proc. Roy. Soc.*, lxxiv., 446), from the density of nitrous oxide under very small pressures, found $N_2O = 43.996$, whence $N = 13.998$.

Guye and Davila (*Comptes Rendus*, cxli., 826) prepared nitric oxide by three different methods, and determined its density. The weight of one litre at Geneva, under normal conditions, is given below. The three columns relate to the three preparations.

1.	2.	3.
1.3406	1.3403	1.3399
1.3402	1.3398	1.3403
1.3401	1.3400	
1.3407	1.3408	
1.3398	1.3402	
1.3402	1.3402	

If the weight of one litre of oxygen is 1.4290 grms., the ratio $NO : O_2$ gives $NO = 30.012$. Corrected by physico-chemical methods, $N = 14.006$ to 14.010 , according to the method employed. (For the method of correction by critical constants, see Guye, *Journ. Chim. Phys.*, iii., 321).

Nitric oxide was also the substance chosen by R. W. Gray (*Journ. Chem. Soc.*, lxxxvii., 1601) for his determinations of the atomic weight of nitrogen. First, its density was determined in comparison with oxygen, by weighing both gases in the same bulb under corresponding conditions. The following weights were observed at Bonn, where the bulb was filled at 0° and 760 m.m.

NO.	Series I.	O_2 .
0.35845		0.38230
0.35852		0.38229
0.35851		0.38227
0.35849		0.38225
0.35848		0.38226
0.35856		0.38230
	Mean ..	0.38228
0.35851	Series II.	
0.35848		
0.35852		
0.35850		

Mean .. 0.35851

Supplementary Determinations.

(Made in London, but corrected to the latitude of Bonn).

0.35848
0.35855

The direct ratio between these weights is $O_2 : NO = 32 : 30.010$, whence $N = 14.010$. Corrected by the method of limiting densities, $N = 14.004$; by the critical constants, 14.008 . Mean value, $N = 14.006$.

Gray effected the gravimetric analysis of nitric oxide by burning finely-divided nickel in the gas. Two sets of determinations were made with nickel from different sources. In the first series, occluded nitrogen in the resultant nickel oxide was determined, and a correction for it was applied. In the second series the occluded gas was

expelled by heating. Only the *corrected* weights are given below.

Weight NO.	Weight O.	Weight N.
Series I.		
0.31384	0.16729	—
0.64304	0.34300	0.29920
0.50672	0.27025	—
Series II.		
0.54829	0.29221	—
0.61862	0.32981	0.28885
0.62622	0.33401	0.29234
0.62128	0.33111	—
0.54469	0.29029	0.25432
0.52001	0.27715	0.24270
0.62103	0.33103	0.28998

From these weights the following values for the atomic weight of nitrogen are derived:—

	Ratio NO : O ₂ .	Ratio N ₂ : O ₂ .	Ratio NO : N ₂ .
I.	14.016	—	—
	13.996	13.999	14.001
	14.000	—	—
II.	14.022	—	—
	14.011	14.013	14.015
	13.998	14.004	14.009
	14.021	—	—
	14.009	14.017	14.014
	14.020	14.011	14.003
	14.017	14.012	14.011
Mean of all	14.010		

The gas remaining after the combustion of the nickel was pure nitrogen, and two density comparisons of it with oxygen were made:—

Weight N ₂ .	Weight O ₂ .
0.32286	0.36889
0.32275	0.36879
Mean .. 0.32280	0.36884

From direct comparison of these figures, $N = 14.003$. Corrected by the method of limiting densities, $N = 14.008$. From the mean of all his determinations Gray puts $N = 14.0085$, or, rounded off, 14.01.

The agreement between all these new values for N , whether gravimetric or physico-chemical, is very striking. In a very complete summary of all the data relative to the atomic weight of nitrogen, Guye has discussed the sources of error in the different methods of determination, and has made it quite clear that the true figure cannot exceed 14.01 (*Bull. Soc. Chim.*, August, 1905, with independent pagination; another paper by Guye is in *Comptes Rendus*, cxi., 1387). The Stas value, 14.04, seems certainly to be high, although the source of error in it remains to be ascertained. The higher value, however, was obtained in two analyses of silver trinitride, AgN_3 , by A. W. Browne (*Journ. Am. Chem. Soc.*, xxvii., 554), who promises further determinations. In Guye's summary, the possibility of a change in the atomic weight of silver is indicated; but that, so far, is only a suggestion. Hinrichs (*Comptes Rendus*, cxi., 1590), in a brief criticism of recent work, argues in favour of $N = 14$.

Chlorine.

Two important memoirs on the atomic weight of chlorine appeared during 1905. First, Dixon and Edgar (*Phil. Trans.*, Series A, ccv., 169) have effected a direct comparison between hydrogen and chlorine. Hydrogen was weighed in palladium. Chlorine, prepared by the electrolysis of fused silver chloride, was weighed in liquid form. The two elements, with chlorine slightly in excess, were made to unite in a glass bulb; the excess of chlorine remaining after union was caused to liberate iodine from a solution of potassium iodide, and then determined by titration with

sodium thiosulphate. The corrected data, reduced to a vacuum standard, are given in the following table:—

Weight H.	Weight Cl.	Atomic Weight Cl.
0.9993	35.1666	35.191
1.0218	35.9621	35.195
0.9960	35.0662	35.207
1.0243	36.0403	35.185
1.0060	35.4144	35.203
0.9887	34.8005	35.198
1.0159	35.7639	35.204
1.1134	39.1736	35.184
1.0132	35.6527	35.188

Mean 35.195 $\pm$ 0.0019

This, of course, refers to hydrogen as unity; if $O = 16$, $Cl = 35.463$. Additional determinations, to include the weight of the hydrochloric acid produced, are promised.

These determinations by Dixon and Edgar have the peculiar merit of directness. Chlorine is referred to one of the fundamental standards, without the intervention of any other element, although the method employed is one of great experimental difficulty, and therefore subject to undiscovered errors. On their face, however, the results are entitled to receive very high weight.

The work of Richards and Wells, on the other hand, is indirect, at least so far as the atomic weight of chlorine is concerned (*Journ. Am. Chem. Soc.*, xxvii., 459; *CHEMICAL NEWS*, xciii., p. 175; original in Publication 28 of the Carnegie Institution). In their research the synthesis of silver chloride was effected by two distinct processes, and from the data so obtained—the atomic weight of silver being assumed—that of chlorine was calculated.

Some of the syntheses were performed by dissolving silver in nitric acid, precipitating as chloride, and weighing the latter in a Gooch crucible. In other cases the nitrate was converted into chloride in a quartz dish, dried therein, and weighed without transfer of material. All weights, of course, were reduced to a vacuum, and many corrections were carefully determined and applied. The corrected results from two series are as follows. (For details, the original memoir must be consulted). The brackets indicate sub-series involving the use of different samples of silver.

Weight Ag.	Weight AgCl.	Ratio, 100 Ag : AgCl.
Preliminary Series.		
9.06483	12.04365	132.861
8.39217	11.14985	132.860
5.37429	7.14056	132.865
8.08222	10.73869	132.868
7.08517	9.41362	132.864
7.97715	10.59837	132.859
8.11978	10.78767	132.857
8.53452	11.33907	132.861
6.73284	8.94511	132.858
8.91366	11.84240	132.857
9.72295	12.91769	132.858
8.63961	11.47862	132.860
11.13795	14.79849	132.865

Mean 132.861

Final Series.

7.24427	9.62508	132.865
8.30502	11.03484	132.870
7.29058	9.68676	132.867
8.58472	11.40614	132.866
8.01318	10.64648	132.862
9.77160	12.98335	132.868
7.98170	10.60528	132.870
11.49983	15.27964	132.868
6.25318	8.30834	132.866
7.72479	10.26360	132.866

Mean 132.867
Stas found .. 132.848

From the final series, if $Ag = 107.92$, $Cl = 35.470$. If $Ag = 107.93$, $Cl = 35.473$. The authors indicate a preference for the lower value for silver. In either case the value for chlorine is higher than the hitherto accepted 35.455; and its adoption will compel many corrections to be made in the general atomic weight table. The research of Richards and Wells is a model of painstaking accuracy.

From the density and critical constants of hydrochloric acid, Guye (*Comptes Rendus*, cxl., 1241) finds the molecular weight $HCl = 36.484$, whence $Cl = 35.476$. A new determination of the density of chlorine gas has lately been published by Treadwell (*Zeit. Anorg. Chem.*, xlvii., 446) but not yet applied to the calculation of its molecular weight.

(To be continued).

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

PART I. (continued).—PREPARATION OF THE SOLUTION
(INCLUDING THE DETECTION OF OSMIUM, SILVER,
AND LEAD).

By ARTHUR A. NOYES.

(Continued from p. 160).

Confirmatory Experiments and References.

P. 1, N. 4.—The following minerals or products left a large residue when 1 gm. was treated with HNO_3 (1.20) as above described:—Galenite, PbS ; emery, Al_2O_3 ; chromite, $FeCr_2O_4$; zircon, $ZrSiO_4$; pyrolusite, MnO_2 ; lead dioxide, PbO_2 ; cinnabar, HgS ; fluorite, CaF_2 ; fused silver chloride, $AgCl$; and Prussian blue, $Fe_4(FeC_6N_6)_3$. One gm. of fused $PbCrO_4$ dissolved on three successive digestions with 20 c.c. HNO_3 (1.20). One gm. of precipitated $CaSO_4$ dissolved upon one treatment with 10 c.c. HNO_3 (1.20), after diluting with 20 c.c. water, and remained in solution upon cooling.

P. 3, N. 1.—In several experiments 500 m.grms. Pb as $Pb(NO_3)_2$ were treated with 5 c.c. commercial HF containing some H_2SO_4 . The mixture was then treated according to P. 3 and P. 5. A residue consisting of $PbSO_4$ always remained, as was proved by decomposing it with Na_2CO_3 and testing for its constituents.

Three c.c. pure 43 per cent HF solution were mixed with 10 c.c. HCl (1.03) in one experiment and with 20 c.c. HCl (1.02) in another; then 1 c.c. 10 per cent $BaCl_2 \cdot 2H_2O$ solution was added; no precipitate (of BaF_2) separated even on standing ten minutes. One drop (0.04 c.c.) H_2SO_4 (1.20) was then added; a precipitate formed immediately.

P. 3, N. 3.—To 5 c.c. portions of 43 per cent HF solution 1 per cent solutions of various elements were gradually added until a permanent precipitate was produced, waiting two or three minutes after the addition of each half m.grm. or m.grm. The number of m.grms. that had to be added were as follows:—Li, 5; Mg, 2; Ca, 0.5; Sr, 8; Ba, 30; Pb, 0.5; Bi, 0.5; Th, 0.5; Ce, 0.5; Pr, 0.5; Nd, 0.5; La, 0.5; Y, 0.5; and Er, 0.5.

P. 3, N. 4.—Two m.grms. Ta as Ta_2O_5 were heated for fifteen minutes on the water-bath with 5 c.c. 43 per cent HF solution, and the solution was then evaporated to complete dryness, in one experiment twice with the addition of 2 c.c. HNO_3 (1.42), and in another, once without this addition. The residues were then tested for tantalum by the KHF_2 test as described in Part II. In the experiment in which the HNO_3 was added, a satisfactory test was obtained; in the other experiment, no test whatever was obtained, showing that the 2 m.grms. Ta were completely volatilised in the latter case. One m.grm. Ti as H_2TiO_3 was dissolved in 5 c.c. HF , and the solution was then evaporated to complete dryness, in one case twice with the addition of 2 c.c. HNO_3 (1.42), in another once without

that addition. The residues were treated with 20 c.c. H_2O_2 and 2 c.c. HCl . No colour was obtained in the former experiment; a colour corresponding to at least 0.5 m.grm. in the latter.

A mixture of 1 m.grm. Se, 1 m.grm. As, 1 m.grm. Hg, and 1 m.grm. Sb was evaporated to dryness with HNO_3 and treated according to P. 3 (without the addition of SiO_2), and subsequent procedures until the final tests for these four elements were reached. Very satisfactory tests for all of them were obtained, showing they were not volatilised in the HF evaporation.

About 40 m.grms. GeO_2 , made by heating the metal with HNO_3 (1.20) till it was dissolved, evaporating the solution to dryness, and heating the residue at 120° in a platinum dish to a constant weight, were treated with 5 c.c. HF and 5 c.c. HNO_3 (1.42); the solution was then evaporated to dryness, and the residue heated to 120° , and weighed; the change in weight was only 0.1 m.grm.

P. 3, N. 5.—100 m.grms. Ta as Ta_2O_5 were dissolved in 5 c.c. HF and evaporated to dryness three times with 3 c.c. HNO_3 (1.42); the residue was then boiled with 15 c.c. HNO_3 (1.05) for one minute; the solution after filtration, neutralisation with NH_4OH , and addition of $HC_2H_3O_2$ and $CaCl_2$ gave no precipitate, showing the absence of HF .

The same experiment was repeated with 100 m.grms. Nb as Nb_2O_5 and with 100 m.grms. Ti as H_2TiO_3 with just the same result.

P. 3, N. 6.—Fifty m.grms. Ca as $Ca(NO_3)_2$ were digested on a water-bath fifteen minutes with 5 c.c. HF ; 5 c.c. HNO_3 (1.42) were added, and the solution was evaporated to complete dryness, the residue was covered with HNO_3 (1.42), and this was evaporated off; 10 c.c. HNO_3 (1.05) were then added, and the solution was made alkaline with NH_4OH ; only a very slight turbidity resulted.

The same experiment was repeated several times with 200 and 500 m.grms. Ca; in every case a residue remained, or a milky colloidal solution resulted upon treatment with HNO_3 (1.05).

500 m.grms. Pb as $Pb(NO_3)_2$ and 500 m.grms. Bi as $Bi(NO_3)_3$ were treated in separate experiments in the manner just described; a perfectly clear solution was produced on adding the 10 c.c. HNO_3 (1.05).

A mixture of 250 m.grms. Mg, 250 m.grms. Ba, 250 m.grms. Sr, and 250 m.grms. Li were treated in the same manner; a perfectly clear solution resulted on the addition of the HNO_3 (1.05), and this gave no precipitate on neutralising with NH_4OH , and adding $HC_2H_3O_2$ and $CaCl_2$.

P. 3, N. 7.—In regard to the solubility in HF of the oxides of the tungsten and niobium groups, see C. E. on P. 6, N. 1.

P. 3, N. 8.—500 m.grms. Ca, as $Ca(NO_3)_2$, were treated according to P. 3 with addition of SiO_2 , and then by P. 5 and 6; no residue whatever remained after the final treatment with HF . This experiment was repeated many times with the same result.

250 m.grms. Y, 250 m.grms. Ce, 500 m.grms. Nd, a mixture of 50 m.grms. Er, and 50 m.grms. Y, and a mixture of 500 m.grms. Nd, and 500 m.grms. La (all as nitrates) were treated in separate experiments according to P. 3, 5, and 6; in all of these cases there was no residue, or only a very small one (of 2—3 m.grms.) after the final treatment with HF .

Portions of 250 m.grms. Th, and of 50 m.grms. Th, as $Th(NO_3)_4$, were treated according to P. 3, 5, and 6; on treatment with HF a dense crystalline residue estimated at one-tenth the original amount remained. This experiment was repeated many times with the same result.

P. 3, N. 11.—100 m.grms. Ta, as Ta_2O_5 , were dissolved in 5 c.c. HF , and evaporated to dryness three times with 3 c.c. HNO_3 (1.42); the residue was then boiled with 15 c.c. HNO_3 (1.05) for one minute; after filtration the solution gave a heavy precipitate with NH_4OH . The experiment was repeated with the modification that the residue was heated at 120° for seventy minutes after the

* From the *Technology Quarterly*, xvi., No. 2.

three evaporations; the HNO_3 (1.05) solution then gave no precipitate whatever with NH_4OH . This shows that dehydration is necessary and sufficient to make the Ta_2O_5 insoluble.

The same experiment was twice made with 500 m.grms. Sn; the HNO_3 solution of the residue which was not dehydrated gave a large precipitate with NH_4OH , and with H_2S (after evaporation with HCl).

P. 5, N. 1.—A series of experiments was made in which solutions of various elements were evaporated to dryness with HNO_3 , and the residues were heated in a hot closet for one hour, and then boiled gently with 5 c.c. HNO_3 (1.20) for five minutes; the solutions thus obtained were diluted with 15 c.c. water, heated to boiling, filtered, and evaporated to dryness in crucibles, which were then gently ignited and weighed. It was found in this way that from a residue of 30 m.grms. Sn, as H_2SnO_3 , only 0.3 m.grm. dissolved; from one of 70 m.grms. W, as H_2WO_4 , only 1.1 m.grm. dissolved, which was proved to be not tungsten, but some impurity, by its complete insolubility in NH_4OH ; from a residue of 56 m.grms. Ta, as Ta_2O_5 , only 0.4 m.grm. dissolved; from one of 100 m.grms. Nb a few m.grms. dissolved, but on adding NH_4OH to the solution a precipitate formed which dissolved completely in dilute HCl , proving that no niobium dissolved in the HNO_3 ; from a residue of 22 m.grms. Sb, as Sb_2O_5 , 1 m.grm. Sb dissolved on the first treatment with HNO_3 , and 0.9 m.grm. on each of the two following treatments; and from a residue of 85 m.grms. Ti, as H_2TiO_3 , 8 m.grms. dissolved.

750 m.grms. metallic Sn were treated with HNO_3 (1.42), the acid was evaporated off, and the residue heated at 120° for an hour. The residue was then heated for ten minutes with 5 c.c. HNO_3 (1.20), 20 c.c. water added, the solution heated to boiling, and filtered. The filtrate was evaporated with HCl , and tested for tin by means of the HgCl_2 test. No tin was found to be present.

A mixture of 1 m.grm. Ti, 1 m.grm. Ta, 1 m.grm. Nb, 1 m.grm. W, 1 m.grm. Sn, and 1 m.grm. Sb were treated according to P. 3, 5, and 6, and the subsequent procedures (Part II.) for the analysis of the tungsten and niobium groups. Distinct tests were obtained for all the elements except antimony, showing that their oxides remained in the residue insoluble in HNO_3 . (See also T. A., Part II.).

Two m.grms. Sb, as dehydrated Sb_2O_5 , did not dissolve in 5 c.c. boiling HNO_3 (1.20), but it nearly disappeared upon adding 20 c.c. water and boiling. Five m.grms. Sb, as Sb_2O_5 , treated in this way did not dissolve, but almost all of it dissolved upon a second treatment. Ten m.grms. Sb left a large residue even after two treatments.

Fifty m.grms. W, as Na_2WO_4 , and 150 m.grms. PO_4 , as Na_2HPO_4 , were evaporated with HNO_3 , and heated at 120° for two hours; upon adding HNO_3 (1.20), and diluting, everything dissolved.

The same procedure was followed with a mixture of 5 m.grms. W, as Na_2WO_4 , and 50 m.grms. As, as N_3AsO_4 , with the same result.

Ten m.grms. W were precipitated as H_2WO_4 out of a Na_2WO_4 solution by boiling with HNO_3 , and to the mixture 1 c.c. saturated $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ solution was added; the precipitate immediately dissolved.

Fifty m.grms. Sb, as Sb_2O_5 , after dehydration at 120° were treated in one experiment with 10 c.c. half-saturated citric acid solution, and in another experiment with 10 c.c. of a mixture of commercial lactic acid with its own volume of water; upon warming, the residue dissolved.

To 1 m.grm. W, 1 m.grm. Nb, 1 m.grm. Ta, 1 m.grm. Sn, 20 m.grms. Sb (in separate experiments) in solution in 3–5 c.c. HF , 250 m.grms. H_3BO_3 , and 5 c.c. HNO_3 (1.42) were added. The solution was evaporated to dryness, and the residue treated with HNO_3 (1.20), which was then diluted with water. In each case, a small residue of the metallic oxide remained, and this did not go into solution on the addition of 500 m.grms. more H_3BO_3 .

To 1 grm. H_3BO_3 , 5 c.c. HF , and 5 c.c. HNO_3 (1.42) were added, and the solution was evaporated to dryness on a water-bath; no residue was left.

A mixture of 500 m.grms. Ti, as TiO_2 , and 500 m.grms. Zr, as $\text{Zr(NO}_3)_4$, was dissolved in HF , and evaporated to complete dryness four times. It was then heated at 120° for two hours. The residue was treated twice with HNO_3 and water according to the procedure. On the second treatment it went almost entirely into solution, showing that zirconium causes even large quantities of titanium to dissolve.

P. 5, N. 3.—500 m.grms. Mo, as MoO_3 , were dissolved in HF , and following P. 3, the solution was evaporated three times with HNO_3 (1.42), and heated at 120° for an hour. The residue was twice heated with 5 c.c. HNO_3 (1.20), which was afterwards diluted with 20 c.c. water. After the two treatments about one-third of the molybdenum remained undissolved.

The experiment was repeated with 100 m.grms. Mo. A fairly large residue remained after the first treatment of the dehydrated residue with HNO_3 , but only a very small one (2–3 m.grms.) after the second treatment.

In regard to Mo in presence of W or Sn, see T. A., Part II.

A mixture of 200 m.grms. metallic Sb and 50 m.grms. Bi, as $\text{Bi(NO}_3)_3$, was treated with HNO_3 (1.20), evaporated to dryness, and heated at 120° . The residue was heated ten minutes with 5 c.c. HNO_3 (1.20), 20 c.c. water were added, and the mixture was heated to boiling and filtered. The residue was washed thoroughly with hot water and dissolved in HCl (1.20). To the solution NH_4OH and $(\text{NH}_4)_2\text{S}$ were added. Complete solution took place.

The experiment was repeated with a mixture of 500 m.grms. Sb and 500 m.grms. Bi. Even though the dehydrated residue was twice treated with HNO_3 , and thoroughly washed with HNO_3 (1.05), a large black precipitate of Bi_2S_3 remained after adding NH_4OH and $(\text{NH}_4)_2\text{S}$ to the HCl solution of the HNO_3 residue.

A mixture of 50 m.grms. Se, as SeO_2 , and 200 m.grms. Sb, as SbCl_3 , was evaporated three times with HNO_3 , and the residue heated at 120° . It was then treated with HNO_3 and water in the usual manner, and thoroughly washed with water. The undissolved residue was treated with HF , HCl , and H_2SO_3 . The black precipitate which separated was boiled with HNO_3 , the solution distilled with HBr , and the distillate treated with H_2SO_3 . A red precipitate of Se, amounting to perhaps 5 m.grms., separated.

In regard to ThF_4 , see C. E. on P. 3, N. 8.

GeO_2 was made by heating the metal with HNO_3 (1.42), evaporating with HF and then with HNO_3 , and dehydrating at 120° ; the residue, which then weighed 110 m.grms., was boiled one minute with 5 c.c. HNO_3 (1.20), then 20 c.c. water were added, the mixture was boiled again, and filtered, and the filtrate was evaporated and the residue heated at 120° and weighed; it weighed 89 m.grms., showing that 21 m.grms. had dissolved. This residue of 89 m.grms. was then treated again in the same manner; this time 28.5 m.grms. dissolved.

Fifty m.grms. Se, as SeO_2 , and 200 m.grms. metallic Sn were treated in the same manner, except that the residue insoluble in HNO_3 was dissolved in HBr , the solution distilled, and the distillate treated with H_2SO_3 and KI ; a large red precipitate of Se (of perhaps 10 m.grms.) was obtained.

Fifty m.grms. Te, as TeO_2 , with 200 m.grms. metallic Sn in one experiment, and with 200 m.grms. Sb, as SbCl_3 , in another, were treated in the same manner, except that the residue insoluble in HNO_3 was dissolved in HF , the solution evaporated with HCl , and treated with H_2SO_3 ; a large black precipitate of Te formed in each case.

In regard to Se and Te in presence of elements of the tungsten and niobium groups (see also T. A., Part II.).

Fifty m.grms. Zr, as $\text{Zr(NO}_3)_4$, with 600 m.grms. PO_4 , as Na_2HPO_4 , in one experiment, and with 800 m.grms. As, as As_2O_3 , in another, were evaporated with HNO_3 , and the residue heated at 120° . On treatment with HNO_3 (1.20) and dilution, a large residue remained, and the solu-

tion gave a large precipitate with NH_4OH , showing that the zirconium divided itself between the two.

The experiment was repeated with a mixture of 500 m.grms. Zr and 50 m.grms. As; scarcely any residue remained after the treatment with HNO_3 .

The last experiment was repeated, substituting 500 m.grms. Ti dissolved in HF for the 500 m.grms. Zr. The HNO_3 extract of the residue, after evaporation with 1 c.c. H_2SO_4 , gave, upon addition of one-fifth its volume of HCl (1:2) and saturation for one hour at the boiling temperature, a considerable precipitate of As_2S_5 . The residue after similar treatment also yielded a precipitate of As_2S_5 which was somewhat smaller than that obtained from the solution, showing that arsenic divides itself between the residue and solution when titanium is present.

250 m.grms. Th, as $\text{Th}(\text{NO}_3)_4$, and 250 m.grms. PO_4 , as Na_2HPO_4 , were evaporated with HNO_3 , and heated at 120° for two hours. On heating on a water-bath with 10 c.c. HNO_3 (1:20), everything dissolved except a few hard particles. On adding 20 c.c. cold water a large flocculent precipitate formed, and upon then heating on the steam-bath the solution gelatinised.

Fifty m.grms. V, as $(\text{NH}_4)_3\text{VO}_4$, and 500 m.grms. Sn, as SnCl_2 , were evaporated repeatedly with HNO_3 , and the residue was heated at 120° , and then treated with HNO_3 (1:20). A bright yellow residue remained, which upon treatment with HCl (1:20) yielded a blue-green solution, and the HNO_3 solution was of a brown colour, thus showing that the vanadium was divided.

P. 5, N. 4.—See C. E. on P. 3, N. 3, and T. A. Part II.

P. 5, N. 5.—500 m.grms. Zr, Th, Te, Bi, Al, Cr, Pb, and 75 m.grms. Ga, as nitrates, were, in separate experiments, evaporated to dryness with HNO_3 , and the residue heated for an hour at 120° ; this was then heated with 5 c.c. HNO_3 (1:20), and finally with 20 c.c. water; everything dissolved in this single treatment; the gallium did not do so, however, until the 20 c.c. water were added. The experiment was repeated with 500 m.grms. V, as $(\text{NH}_4)_3\text{VO}_4$, dissolved in HF, and with 500 m.grms. Fe, as FeCl_3 ; two treatments of the dehydrated residue with HNO_3 and water were necessary and sufficient to produce complete solution.

A mixture of 500 m.grms. Ti, as TiO_2 , and 500 m.grms. Zr, as $\text{Zr}(\text{NO}_3)_4$, was dissolved in HCl , and the mixture evaporated three times with the addition of HNO_3 (1:42), and then heated at 120° for two hours. The residue was treated twice according to the procedure with HNO_3 (1:20) and water, and the residue still remaining was dissolved in HF, the solution evaporated with 1 c.c. H_2SO_4 (1:84), and then diluted with 100 c.c. H_2O_2 , and 1 c.c. Na_2HPO_4 was added. No precipitate of $\text{Zr}_3(\text{PO}_4)_4$ separated on twenty minutes' standing.

A mixture of 50 m.grms. each of Al, Ni, V, Cr, Be, and Zr was treated in the manner just described; everything dissolved on the first treatment with HNO_3 .

The C. E. on P. 3, N. 8, made with the rare earth elements other than thorium show that even large quantities of these dissolve completely upon the treatment with the HNO_3 .

Twenty m.grms. Au, as AuCl_3 , were four times evaporated with a little HNO_3 (1:42), and then heated at 120° for two hours. On heating with 5 c.c. HNO_3 (1:20) all but 2—3 m.grms., consisting of a metallic powder, dissolved.

P. 6, N. 1.—500 m.grms. Sn, as metal, of Sb, as metal, of W, as Na_2WO_4 , of Ti, as TiO_2 , of Mo, as MoO_3 , of Te, as TeO_2 , and 30 m.grms. Ge, as GeO_2 , were treated in separate experiments with HNO_3 , the liquid evaporated off, the residue heated at 120° for an hour or more, and then heated on a steam-bath for five minutes with 5—10 c.c. HF; a clear or slightly opalescent solution resulted in every case except that of tin. Twenty c.c. cold water were then added to each solution; the tin solution became clear, and all the others remained so.

To 5 c.c. HF, diluted with 25 c.c. cold water, 1 per cent Bi solution was added, 1 m.grm. Bi at a time,

until a permanent precipitate formed; 6 m.grms. Bi were required.

To a HF solution of 500 m.grms. Sn, as SnO_3H_2 , 400 m.grms. PO_4 , as Na_2HPO_4 , were added, the mixture evaporated to dryness three times with HNO_3 , and the residue heated an hour at 120° ; then it was heated with 5 c.c. HF, and finally 20 c.c. water were added; a large residue of at least 100 m.grms. remained, and this did not dissolve on a second treatment with HF and water.

See also C. E. on P. 6, N. 3, in those cases where the minerals contain the elements of the tungsten and niobium groups.

P. 6, N. 2.—One grm. of each of the following substances was treated according to P. 1, 3, 5, and 6, with the result that a large residue was left on the final treatment with HF:—Galenite, PbS ; cinnabar, HgS ; molybdenite, MoS_2 ; pyrolusite, MnO_2 ; lead dioxide, PbO_2 ; emery, Al_2O_3 ; chromite, FeCr_2O_4 ; cassiterite, SnO_2 ; rutile, TiO_2 ; fused silver chloride, AgCl ; cyanite, Al_2SiO_5 ; tourmaline, $\text{Al}_2\text{O}_3 \cdot (\text{Fe}, \text{Mn}, \text{Mg})_2\text{O} \cdot (\text{K}, \text{Na}, \text{Li})_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{F}$; beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$; zircon, ZrSiO_4 ; monazite, $(\text{Ca}, \text{La}, \text{Pr})_{15}(\text{PO}_4)_{10}\text{Th}_2\text{P}_2\text{O}_9$.

That andalusite and cyanite, Al_2SiO_5 , and tourmaline are not decomposed by HF is stated by Jannasch in his "Gewichtsanalyse." 1897, 231, 233.

P. 6, N. 3.—One grm. of each of the following substances in the form of an impalpable powder was treated according to P. 1, 3, 5, and 6, with the result that no residue, or only a very small one amounting to 1—5 m.grms., was left on the final treatment with HF:—Magnetite, Fe_3O_4 ; menaccanite, $\text{FeTiO}_3 \cdot \text{Fe}_2\text{O}_3$; pyrite, FeS_2 ; pyrrhotite, Fe_7S_8 ; chalcocopyrite, CuFeS_2 ; stibnite, Sb_2S_3 ; niccolite, NiAs ; fluorite, CaF_2 ; cryolite, Na_3AlF_6 ; gypsum, CaSO_4 ; wollastonite, CaSiO_3 ; tremolite, $(\text{Ca}, \text{Mg})\text{SiO}_3$; titanite, CaTiSiO_5 ; orthoclase, $\text{K}_2\text{Al}_2\text{Si}_6\text{O}_{16}$; labradorite, $(\text{Ca}, \text{Na}_2)\text{Al}_2\text{Si}_3\text{O}_{10}$; garnet,—

$(\text{Ca}, \text{Mg}, \text{Mn}, \text{Fe})_3\text{Al}_2\text{Si}_3\text{O}_{12}$;

gadolinite, $(\text{Y}, \text{Ce}, \text{Be}, \text{Fe})_3\text{SiO}_5$; scheelite, CaWO_4 ; columbite, $\text{Fe}(\text{Nb}, \text{Ta})_2\text{O}_6$; samarskite,—

$(\text{Fe}, \text{Y}, \text{VO}_2)_5(\text{Nb}, \text{Ta})_4\text{O}_{15}$;

and the rocks basalt, obsidian, amphibole, and lava.

P. 7, N. 1.—To 500 m.grms. Pb, as PbSO_4 , successive portions of 5 c.c. HCl (1:20) were added, the solution being boiled after each addition, until the solid all went into solution; 30 c.c. sufficed to produce this result. Ninety c.c. water were then gradually added, keeping the solution at the boiling-point; no precipitate was produced. 800 m.grms. Pb, as PbO_2 , dissolved readily in 30 c.c. HCl (1:20), and remained in solution on adding 90 c.c. water.

To 20 m.grms. BaSO_4 30 c.c. HCl (1:20) were added and the liquid boiled a few minutes; complete solution resulted. Thirty c.c. water were added to the solution kept at the boiling-point, no precipitate formed.

The same experiment was repeated with 100 m.grms. AgCl with the same result.

500 m.grms. fused AgCl in the form of shavings were boiled for three or four minutes with successive 30 c.c. portions of HCl (1:20); the solid all dissolved on the third treatment or in 90 c.c. HCl (1:20).

500 m.grms. Sn, as metal, and 400 m.grms. PO_4 , as Na_2HPO_4 , were evaporated with HNO_3 (1:42), and heated at 120° ; the residue was treated twice with HF and water, as described in P. 6, and the large residue still remaining (amounting apparently to 200 m.grms.) was heated on a steam-bath for ten minutes with 15 c.c. HCl (1:20); complete solution occurred.

P. 7, N. 3.—The following substances, in the form of a fine powder, were submitted, if non-metallic, in quantity of 1 grm. to P. 1, 3, 5, 6, and 7; if metallic, in quantity of 0.5 m.grm. to P. 4, 5, 6, and 7, with the result that a large residue, amounting to at least one-half of the original substance, remained in every case:—Molybdenite, MoS_2 ; emery, Al_2O_3 ; chromite, FeCr_2O_4 ; cassiterite, SnO_2 ; rutile, TiO_2 ; thorium fluoride, ThF_4 ; Prussian blue, $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$; cyanite, Al_2SiO_5 ; tourmaline; zircon,

ZrSiO₄; monazite, mainly Th₃(PO₄)₄; metallic rhodium, Rh; metallic iridium, Ir; Ural Mts. platinum ore, Pt, Pd, Os, Ir; Ural Mts. osmium-iridium, Os, Ir; crude ruthenium, Ru; ferrochrome, Cr, Fe; ferrosilicon, Fe with 13 per cent Si.

P. 8, N. 1.—Barium sulphate, tourmaline, cyanite, and allied silicates are analysed quantitatively by decomposition with Na₂CO₃. (See Classen, "Quantitative Analysis," Harriman's translation, pp. 62, 204).

330 m.grms. of cyanite, constituting the residue left after treatment of 1 grm. of the mineral by P. 1, 3, 5, and 6, were fused with 7 grms. Na₂CO₃ (this large quantity being necessary to produce a fluid fusion); on treatment first with hot water, and then with HCl, everything dissolved.

One grm. of each of the following substances as an impalpable powder was treated by P. 1, 3, 5, 6, and 7, and the residue was fused with Na₂CO₃ as directed in P. 9:—Emery, Al₂O₃; rutile, TiO₂; cassiterite, SnO₂; monazite, Th₃(PO₄)₄, &c.; and zircon, ZrSiO₄. A large residue was left upon extracting the fusion with water and adding HCl to the residue (P. 10, 11).

The residues undecomposed by Na₂CO₃, obtained in the preceding experiment, were fused with K₂S₂O₇ by P. 12; emery, rutile, zircon, and monazite went completely into solution on adding the fusion to water, or upon treating the residue with H₂SO₄ (1:20). In the case of cassiterite, a large residue (450 m.grms.) was left undissolved.

P. 8, N. 2.—500 m.grms. of each of the following substances, reduced to a fine but far from impalpable powder, were first treated for from ten to thirty minutes with strong aqua regia, and the residues were then introduced into a nickel crucible containing 5 grms. Na₂O₂ in a state of fusion, and the fusion was maintained for from five to twenty minutes;—Molybdenite, MoS₂; carborundum, SiC; ferrosilicon, Fe with 13 per cent Si; ferrochrome, Fe:Cr; Ural Mts. platinum ore, Ural Mts. osmium-iridium, pure metallic iridium, crude metallic ruthenium, and (100 m.grms.) pure metallic rhodium. All of these substances except the platinum metals reacted violently with the Na₂O₂, with the production of much light and heat. Complete solution resulted in case of all the substances upon adding to the fused mass 75 c.c. water, neutralising with HCl, adding a moderate excess of it and heating (except that in case of carborundum a small flocculent precipitate of SiO₄H₄ separated).

P. 12, N. 1.—One grm. monazite was treated with HF and HNO₃ (P. 2 and 5), and the residue was fused with K₂S₂O₇ and H₂SO₄ (P. 12). On adding the mass to water, a flocculent precipitate formed; but this dissolved on decanting the liquid, and adding 10 c.c. H₂SO₄ (1:20).

500 m.grms. Ti, as TiO₂, were fused with 5 grms. K₂S₂O₇ and 4 c.c. H₂SO₄ were added. On adding the mass to 50 c.c. water everything dissolved, and remained in solution upon boiling.

Ten grms. K₂S₂O₇ were heated at a dull red heat in a covered platinum crucible for twenty minutes. The mass was cooled, 2 c.c. H₂SO₄ (1:84) were added, and the mixture heated for fifteen minutes below its boiling-point till a clear fusion resulted. On cooling, about half the mass separated as a compact solid, and the other half remained viscous. On adding 2 c.c. more of H₂SO₄ (1:84), re-heating for ten minutes till a clear fusion was obtained, and then cooling, the mass became viscous, but was so liquid that it could be poured out.

P. 12, N. 3.—The liquid mass obtained in the last experiment was added to 30 c.c. water, two drops HCl (1:20) added, and the solution was then shaken with 1 c.c. Ag. From the colour of the precipitate it was estimated by comparison with the colours obtained with known amounts of platinum, that 2 m.grms. Pt had been taken up from the crucible.

P. 13 N. 1.—See C. E. on P. 8, N. 2, in regard to action of Na₂O₂ on the substances that may be present in a dark coloured or metallic residue.

P. 13, N. 2.—Five grms. Na₂O₂ were fused at a lower red heat for twenty minutes in a 35 c.c. nickel crucible

weighing 17 grms. The crucible, after washing out and drying, had lost 1 grm.

Two grms. Na₂O₂ were fused for twenty minutes on a silver crucible cover; the cover lost 0.9 grm.

In regard to the action of Na₂O₂ on Ni, Fe, Ag, and Pt, see also Dudley (*Am. Chem. Journ.*, 1902, xxviii., 59—66), and Leidié and Quennessen (*Bull. Soc. Chim.*, 1902, [3], xxvii., 179—183).

P. 13, N. 3.—Five grms. Na₂O₂ from Roessler and Hasslacher, N.Y., made from metallic sodium under the Castner patent, was submitted to a qualitative analysis. This quantity contained only about 3 m.grms. Fe and 1 m.grm. Sb as metallic impurities.

P. 13, N. 4.—For the composition of the hydrated oxide of nickel produced, see Dudley (*Journ. Am. Chem. Soc.*, 1896, xviii., 901—902).

P. 13, N. 5.—For the composition of the fusion products of platinum, see Dudley (*Am. Chem. Journ.*, 1902, xxviii., 59); of iridium, Claus (*J. Prakt. Chem.*, 1846, xxxix., 101).

500 m.grms. Ir, as metal, and 500 m.grms. Pt, as metal, were in separate experiments fused in a nickel crucible with 5 grms. Na₂O₂ for seventy-five minutes. The fused mass was treated with 100 c.c. water, and the coal-black residue allowed to settle. The very slightly yellowish solution was decanted, acidified with HCl, and evaporated nearly to dryness; the residue was treated with HCl (1:20); the solution was decanted from the pure white NaCl, and evaporated to dryness with HNO₃; the residue was dissolved in 1 c.c. water, and the solution was saturated with NH₄Cl. In the case of the iridium, only about 1 m.grm. Ir separated as a black precipitate, showing that the fusion product was almost insoluble in water. This is in disagreement with the statement of Leidié and Quennessen (*Bull. Soc. Chim.*, 1902, [3], xxvii., 181), according to which the iridium after fusion dissolves completely in water with production of a deep blue solution. In the case of the platinum, no (NH₄)₂PtCl₆ was obtained. The residue insoluble in water was thoroughly washed, and it was then warmed with HCl (1:20). In the case of the iridium it very quickly dissolved to a clear dark blue solution, which during evaporation changed to a dark red colour. In the case of platinum, a large quantity of a dense yellow residue remained after long boiling with HCl (1:20) and strong aqua regia. The HCl solution, however, contained a large quantity of platinum, as was shown by precipitating it in a pressure bottle with H₂S.

500 m.grms. crude Ru were fused with 5 grms. Na₂O₂, and treated with water in the usual manner. The aqueous solution was dark orange-red, and upon adding HCl to the solution and residue, a clear, very dark red solution resulted.

100 m.grms. commercial Rh were fused with Na₂O₂, and treated with water. The supernatant liquid after the precipitate settled was dark orange-yellow, and it remained so after decanting and acidifying with HCl, but it became colourless on boiling; these results being perhaps attributable to the presence of osmium. The black residue and adhering solution were treated with HCl; in the cold there was a large finely divided cream-coloured residue, but upon heating this almost entirely dissolved, yielding a dark yellow-orange solution.

P. 13, N. 7.—200 m.grms. Os were fused with Na₂O₂, the fused mass treated with water and HCl, and the liquid distilled (as in P. 13); after distilling five minutes, the dark orange distillate was replaced by fresh NaOH; after distilling three minutes longer, a yellow distillate corresponding in colour to that given by 4—5 m.grms. was obtained; on again replacing the distillate and boiling for two or three minutes longer, a colourless distillate giving no precipitate with Na₂S₂O₃, and HCl resulted. Twenty-five c.c. HNO₃ (1:42) were then added to the residual solution, and the distillation continued for ten minutes; the light yellow distillate was then treated with HCl and 2 c.c. saturated Na₂S₂O₃ solution; the precipitate obtained was pure white, showing that the osmium distilled over completely in less than ten minutes, and that the addition of HNO₃ is unnecessary.

P. 13, N. 8.—500 m.grms. crude Ru were fused with Na_2O_2 , the fused mass treated with water and HCl, and the liquid distilled (as in P. 13); a weakly coloured distillate, giving with HCl and $\text{Na}_2\text{S}_2\text{O}_3$ a small precipitate corresponding to 1–2 m.grms. was obtained; this was probably due to a little osmium present in the material used. On further distillation into a new portion of NaOH, the latter remained colourless, showing that the ruthenium does not distil over.

P. 13, N. 10.—In one experiment 200 m.grms. very finely powdered osmium, and in another 500 m.grms. powdered osmium iridium were boiled in a distilling flask with strong aqua regia, and the distillate caught in NaOH solution; in neither case did the distillate give a dark coloured precipitate when tested with $\text{Na}_2\text{S}_2\text{O}_3$ and HCl.

P. 14, N. 1.—That the distillation and test with $\text{Na}_2\text{S}_2\text{O}_3$ will show 0.5 m.grm. Os was proved by experiment.

The distillate obtained by distilling 1 m.grm Ru with dilute H_2SO_4 and KMnO_4 was tested with $\text{Na}_2\text{S}_2\text{O}_3$ by P. 14. A black precipitate was produced.

P. 16, N. 2.—The dense yellow residue of Pt_2O_3 insoluble in HCl and aqua regia, referred to in C. E. on P. 13, N. 5, was allowed to stand in the cold over night under water saturated with H_2S ; it was completely converted to a black sulphide, which dissolved readily in aqua regia.

P. 18, N. 1.—As to the solubility of AgCl in NH_4OH , see Bodländer and Fittig (*Zeit. Phys. Chem.*, 1901, xxxix., 602), Whitney and Melcher (*Journ. Am. Chem. Soc.*, 1903, xxv., 78).

500 m.grms. Pb, as PbSO_4 , were boiled with 20 c.c. NH_4OH (0.90), the mixture filtered hot, the filtrate nearly neutralised with HNO_3 , and then acidified slightly with HCl , and a few drops of K_2CrO_4 added; a considerable yellow precipitate of PbCrO_4 formed. The experiment was repeated with the modification that the NH_4OH solution was cooled before filtering; in this case a precipitate equivalent to only about 0.2 m.grm. Pb resulted.

P. 19, N. 1.—The statement as to the quantity of PbSO_4 dissolved by 15 c.c. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution is based on a direct experiment.

A mixture of 500 m.grms. Ba and 500 m.grms. Sr, freshly precipitated as BaSO_4 and SrSO_4 , was collected on a filter, a portion of 10 c.c. hot $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ reagent was poured several times through the filter, the filtrate was acidified with HCl , and a few drops of K_2CrO_4 were added; no precipitate resulted.

500 m.grms. Sr, as SrSO_4 , were boiled with 20 c.c. of the $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ reagent, filtered while hot, and 30 c.c. of $(\text{NH}_4)_2\text{CO}_3$ added; after standing for ten minutes, a precipitate estimated at 3–5 m.grms. had separated.

For the solubility of SrSO_4 in HCl (1.04) and HNO_3 (1.032) see Fresenius ("Quantitative Analysis," Am. Ed. of 1881, p. 815).

P. 20, N. 1.—500 m.grms. Sr, as freshly precipitated SrSO_4 , were boiled for ten minutes with 10 c.c. saturated Na_2CO_3 solution, the precipitate washed, and then treated with 10 c.c. cold HCl (1.12); it entirely dissolved.

500 m.grms. Ba, as freshly precipitated BaSO_4 , were boiled for five minutes with 25 c.c. saturated Na_2CO_3 solution; the solution was then decanted and the residue boiled for five minutes, with 10 c.c. Na_2CO_3 solution; the solution was again decanted, the residue washed and treated with 10 c.c. HCl (1.02); it dissolved completely.

P. 20, N. 2.—For the theory of the equilibrium between two difficultly soluble salts in the presence of soluble ones with common ions and the results in the case of BaSO_4 and BaCO_3 , see Nernst ("Theoretische Chemie," 3rd Ed., p. 498).

As to the solubility of BaSO_4 , BaCO_3 , SrSO_4 , and SrCO_3 in water, see Kohlrausch and Rose (*Zeit. Phys. Chem.*, 1893, xii., 241). It should not be forgotten, however, that the values given in the cases of the carbonates are much higher than correspond to the true solubility products, owing to the effect of hydrolysis.

(To be continued).

A REVISION OF THE ATOMIC WEIGHTS OF SODIUM AND CHLORINE.*

By THEODORE WILLIAM RICHARDS
 and
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INTRODUCTION.

THE investigation of the atomic weights of the extremely common elements sodium and chlorine was undertaken because of an unaccountable discrepancy which appeared in the composition of a sample of very pure sodic bromide, as compared with the results of Stas. This sodic bromide had been prepared for the purpose of determining the transition temperature of its hydrated crystals; and a preparation which yielded a constant transition point, therefore giving evidence of great purity, nevertheless possessed a perceptibly lower combining weight than that indicated by Stas's results.

Such a discrepancy as this was not to be passed over lightly. It indicated either an unknown constant impurity in our sodic bromide—and hence a possible error in our transition temperature—or else a flaw in the classical work of Stas. When the first cause of disagreement had been carefully sought in vain, the second was pursued.

Thus a physico-chemical investigation demanding great purity of materials led to a quantitative research of unexpected magnitude; and in turn this quantitative investigation depended continually upon physico-chemical methods and considerations. In confirmation of previous work at Harvard, it was found that the physico-chemical conditions of experiment were of as serious import as the purity of the materials, and of far greater significance than an increase in the scale of operations. The essential circumstances here defined must receive consideration in any other research of a similar kind.

It is needless to say that an investigation seeking to test the accuracy of Stas's work is a serious undertaking, for undoubtedly much of his work deserves a rank among the most accurate of quantitative chemical results; certainly he distanced all those who preceded him. Nevertheless, he was by no means infallible, as his long oversight of the solubility of argentic chloride, his difficulty in obtaining colourless ammoniac bromide, the uncertainty concerning the oxygen in his silver, and the recent proof of an important error in his work on iodine,† all testify. Moreover, Stas's work is not to be considered as accurate in proportion to the scale of his experiments, as many have been inclined to suppose. Mere increase in quantity of material can avail nothing if the same physico-chemical error or the same chemical impurity contaminates the whole. Indeed, it is doubtful if beyond a moderate scale of operations increase of quantity decreases even the probability of accidental error. For example, the extreme variations in his work on the synthesis of argentic chloride, in which on the average nearly 200 grms. of the compound were weighed in each analysis, amounted to 0.006 per cent, or 12 m.grms. of material (J. S. Stas, "Oeuvres complètes," Brussels, 1894, i., 341). An accuracy of 0.6 m.grm. with 10 grms. of substance, very easy to attain as far as the collection and weighing of the material is concerned, would have brought him as good agreement. But large quantities have no advantage to offer besides the increased accuracy in weighing and the diminished percentage effect of a given accidental loss of material in transference. For this reason the use of extremely large quantities must rather be considered as evidence of a lack of sound judgment than an index of unusual accuracy. Stas himself acknowledged this by using only about 10 grms. of material in each of his last experiments ("Oeuvres," iii., 503).

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† The work of Ladenburg and Scott has been confirmed by Dr. G. F. Baxter, of Harvard University, whose recent analyses show that the atomic weight of iodine can hardly be lower than 126.97. *Proc. Acad.*, 1904, xli., 419.

Regretfully one must admit that a critical study of the work of Stas upon sodium in particular reveals several possibilities of error, as well as at least one inconsistency. He analysed both the chloride and the bromide; of these salts the former received the greater attention, and will be discussed here in greater detail.

In reviewing his results upon sodic chloride there are two series to be considered, separated by an interval of time of over twenty years. Although at first sight these two series seem to have yielded almost identical results, as a matter of fact they are essentially inconsistent with one another. Both results were obtained by the method of Gay-Lussac, titrating weighed amounts of silver in solution with salt; but at the earlier time the latter was added until all precipitation ceased, while at the later time equivalence was assumed when the supernatant liquid gave equal opalescence with excess of either chloride or silver.

Anyone with experience will recognise that a much higher apparent atomic weight of sodium was to be calculated by the first procedure than by the second, other conditions being the same, and yet the results were almost identical. The immediate inference is, of course, that some other condition or conditions must have varied in order to compensate for the effect of the altered method of titration. This inconsistency, which appears also in his work on potassium and ammonium, has never been explained, and one of the functions of the present work was to account for it.

Among the possible sources of error in Stas's work, the most serious seems to have been the practice of dropping solid salt into the solution of argentic nitrate ("Oeuvres," i., 759; also iii., 479). Of course this practice caused the greater part of the argentic chloride to be precipitated in the presence of a concentrated solution of salt, immediately around the solid—a circumstance tending greatly to promote the occlusion or inclusion of sodic chloride in the precipitate. Stas, in his early work especially, was fully awake to the danger of the occlusion of *argentic nitrate* in this precipitate ("Oeuvres," i., 337); but he seems to have had no fear of occlusion of other salts. In the sequel we shall show that the chloride of silver tends to carry down with it many salts from their concentrated solution, and that the details of treatment determine whether or not these impurities may be removed by washing.

Another possible cause of the discrepancy is to be found in the methods used for preparing the materials. In Stas's earlier investigation, where the analytical end-point was erroneous, greater care was taken in preparing the sodic chloride than in the later experiments. In general, when purifying this salt, he employed violent treatment, and very rarely re-crystallised or in any way fractionated his material afterwards. His favourite method was fusion with ammoniac chloride and ammoniac chlorplatinate. Presumably the ammoniac chloride was used to expel other halogens, and the deposited platinum, Stas believed, carried down silica and alumina with it. Except for these possible advantages, this admixture of foreign materials seems to be a doubtful expedient. In the ten experiments of 1860 ("Oeuvres," i., 365), six different preparations were made, from the following sources:—

1. Sodic carbonate neutralised with hydrochloric acid.
2. Rock salt re-crystallised.
3. Sodic sulphate repeatedly fused with ammoniac chloride.
4. Sodic tartrate re-crystallised and fused with ammoniac chloride.
5. Sodic nitrate, similarly treated.
6. Sodic chlorplatinate re-crystallised and fused.

The final step in every case consisted, as usual, in mixing the salt with ammoniac chloride and ammoniac chlorplatinate, fusing until colourless, and decanting the fused mass from the residue. The ten results agreed almost exactly, indicating that the preparations were, at least, identical; but, of course, the results are all in error, because of the erroneous end-point.

Only two preparations were used in the four experiments of 1881 ("Oeuvres," i., 755). For one of these, impure sodic bicarbonate was neutralised with hydrochloric acid. The salt, after three recrystallisations, was repeatedly fused with ammoniac chloride and chlorplatinate ("Oeuvres," i., 685). By evaporating a solution of the resulting salt with chlorplatinic acid, it was converted into sodic chlorplatinate without fractionation of any kind. About nine-tenths of this material was dissolved in water. Stas assumed that any potassic salt would not then dissolve; but this possibility is by no means excluded. The first lot of crystals from the solution was decomposed and fused, and the resulting sodic chloride used in the first two experiments. A second and third lot were also obtained from the mother-liquor of the first lot. The salt made from the third lot was employed in the fourth experiment of 1881. Thus there were only four crystallisations between the starting point (which was admittedly impure) and the final product; and the first three of these crystallisations were of common salt, isomorphous with potassic chloride. In the third experiment of 1881, the salt was made by neutralising pure acid sodic carbonate and repeatedly fusing with ammoniac chloride in platinum, with no fractionation at all. These specimens were probably less pure than the earlier ones.

Thus it appears that every preparation of Stas was fused in contact with platinum, which was usually in a finely divided "nascent" condition, or at least in the presence of decomposing ammoniac chloride. The question is therefore important whether or not platinum can dissolve in melted salt at the temperature of 800°. We have found that fused salt when pure has but a very slight dissolving effect upon platinum, but in the presence of ammoniac chloride or hydrochloric acid at a red heat in the presence of air a noticeable quantity of platinum is dissolved, as is indicated by the loss of weight of the containing crucible. It seems likely, then, that Stas's material contained traces of platinum, either in a very finely divided state or possibly as a platinum salt; but the amount could hardly have been large. Stas invariably found non-volatile residues in his preparations, consisting of silicates of sodium and calcium, which he discovered by vaporising the salt. These residues usually amounted to about 0.004 per cent.

It is not impossible, however, that yet other impurities might have volatilised with the sodic chloride. In volatilising his salts, Stas used a heat of pure platinum ("Oeuvres," i., 681). It is possible that pure platinum would itself have volatilised appreciably at the temperature required to drive off 10 grms. of salt in half-an-hour.* For either of the two reasons just given, Stas's correction for impurity in his salt would not have been large enough.

These impurities must, however, have been almost equally present in the early and later samples, and could not explain the serious discrepancy between them. At most, however, as we shall show, they could hardly have exceeded 0.01 per cent, an amount much smaller than the discrepancy in question. Our own experience shows that common salt is a substance very easy to prepare in a pure state. Clearly the cause of the discrepancy must be sought elsewhere.

The other essential substance, to be prepared in a pure state, was silver. This Stas prepared in a variety of ways, as is well known; but for all this work the silver was either cast in ingots from under an oxidising flux, or else "granulated" by dropping into water. His criterion of pure silver was the melting of the surface of a button without any apparent irregular expansion as it liquefied, or any flame-colour, and the absence of all specks and spots from the completely melted globule. In all experiments it was reddened in a silver crucible before weighing.

After Dumas had recommended the fusion of silver in a

* See Hall (*Journ. Am. Chem. Soc.*, 1900, xxii., 494); Richards and Archibald (*Proc. Am. Acad.*, 1903, xxxviii., 460); Hulet and Berger (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1512). There seems to be no doubt that platinum is slightly volatile at 1000° in the presence of air. Probably it is not in pure nitrogen.

vacuum, Stas made many experiments upon the occlusion of gases by silver. He carefully investigated the samples of silver used in his atomic weight researches, and also new preparations. He found that fusion in a flux of sodic nitrate introduced a quantity of oxygen, and that bars and blocks were slightly purer than "granulated" silver. In no case was the amount of retained gas found by Stas enough to affect seriously even a very accurate analysis; but as will be shown later, it is probable that he did not find all the oxygen present. An error in Stas's silver would not account for the discrepancy between his results on sodium and ours; for an impurity in the silver would cause his atomic weight of sodium to appear too low, and not too high. On the other hand, the impurity in Stas's silver is undoubtedly the cause of the difference between his atomic weight of chlorine and ours.

From these considerations it was clear that the reason for the incompatibility of the results on sodium was probably to be sought chiefly in the method of analysis rather than in the impurity of the materials. The long-continued search for the causes of discrepancy led finally to a satisfactory explanation of the whole anomaly. In order to make this clear, the details of our own investigation must be recounted.

BALANCE AND WEIGHING.

The Troemner balance which has served in many similar researches was used during most of the present work (*Proc. Am. Acad.*, 1891, xxvi., 242). Successive weighings on it of the same object rarely differed as much as 0.03 mgrm. For a few of the conclusive final experiments a yet more sensitive and perfect balance, especially made for this kind of work by the same maker, was used.

The Sartorius weights were standardised from time to time by the method devised by one of us (Richards, *Journ. Am. Chem. Soc.*, 1900, xxii., 144). It was found as usual that the larger gold-plated and platinum-plated brass weights very slightly changed from time to time, although the smaller platinum weights did not. All weighings were made by substitution. Furthermore, the major portion of the substituted tare consisted of a counterpoise exactly similar to the crucible, tube, or boat which was being weighed. Thus the weights required were never large in amount, and errors due to changes in meteorological conditions were avoided. The method of recording and checking the weights is given in another place (Richards, *Proc. Am. Acad.*, 1895, xxxi., 175; *Zeit. Anorg. Chem.*, 1895, x., 19).

While these obvious particulars are given here for the sake of completeness, it must be remembered that accuracy of weighing is easily attained. The great errors in chemical quantitative work are usually not in the weighing, but are due rather to impurities in the substances weighed or incompleteness or irregularity of reaction. Only in a few cases, with large vessels, was it necessary to use a telescope for reading the vibrations, the observer being in another room and looking through an intervening glass door.

The balance-room devoted to these most accurate determinations was kept at a very constant temperature, being wholly inside a private laboratory whose air temperature was regulated by a delicate thermostatic attachment to its heating apparatus. The balance-room itself had neither heating apparatus nor outside windows. This question of constancy of temperature is of the most vital importance in the weighing of large vessels.

In reducing weights in air to weights in vacuum, the densities at about 20° were assumed to be as given below. The value for silver proceeds from Stas, and was checked by one determination by us of the purest silver (sample W, described later). The value for the brass weights refers to the gold-plated Sartorius weights used in all but a very few of the experiments; the other set had a slightly higher density, of which account was taken. The correction for 1.000 grm. of substance weighed in dry air at 20° and 760 m.m. is stated for each substance.

Substance.	Density at 20°.	Correction for 1 grm. of substance, 20° 760 m.m.
Silver	10.49	- 0.000029
Sodic chloride ..	2.14	+ 0.000018
Silver chloride ..	5.56(a)	+ 0.000073
Weights	8.40	—

(a) Richards and Stull, in an investigation as yet unpublished.

Especially when sodic chloride or silver chloride was weighed the temperature and barometric pressure were recorded at the time of weighing. In case of significant variations of temperature or pressure the corrections were changed accordingly. The correction is computed as follows:—

Correction = w (volume of 1 grm. of substance - volume 1 grm. of weights), where w is the weight of 1 c.c. of air at the given temperature and pressure. The following small table contains a sufficiently accurate statement of this value in convenient form for use with a logarithmic slide rule.

Value of w in Grms.

Temperature (°C).	750 m.m.	760 m.m.	670 m.m.
14°	0.001214	0.001230	0.001246
16°	0.001205	0.001221	0.001237
18°	0.001197	0.001213	0.001229
20°	0.001189	0.001204	0.001220
22°	0.001181	0.001196	0.001212
24°	0.001173	0.001188	0.001204

If the air is completely saturated with water vapour the above values should be decreased by 0.000008 at 14°, 0.000010 at 20°, and 0.000013 at 24°. But since the air of our balance cases was certainly less than a quarter saturated with moisture, any correction on this account would have been supererogatory.

(To be continued).

NOTICES OF BOOKS.

Practical Exercises in Chemistry. By G. C. DONINGTON, M.A. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1906.

THIS book will be found a most valuable aid to the teacher of large classes, for it is one that may safely be put into the hands of the pupil, and may be trusted to give him sufficient—but not superfluous—instructions for his experimental work, and to develop in him the spirit of research. It is undoubtedly one of the best of its kind that we have come across, and can be thoroughly recommended, especially for the use of older students. The subject-matter includes all that is required for the examination in chemistry of the London University Matriculation. The first four chapters are introductory, dealing with the measurement of volume, capacity and density, and simple chemical operations; then the properties and behaviour of common materials, rocks and earths, salts, acids, &c., are taken up, followed by the study of rusting and burning; this order possesses many advantages over the older plan of performing experiments on oxidation at the very beginning of the study of practical chemistry; the learner's interest in the subject is thoroughly awakened, and when he approaches the more difficult work he is much better equipped to profit by it.

Third Treatise on the Effects of Borax and Boracic Acid on the Human System. By Dr. OSCAR LIEBREICH. Translated from the German. London: J. and A. Churchill. 1906.

THE object of this treatise is to review and criticise Dr. Wiley's report, which was issued in 1904, on the influence of boron compounds on health and digestion. Dr. Liebreich does not agree with the conclusions drawn from

the Washington experiments, and in many respects it must be confessed that he is justified in the attitude he adopts towards the results of the experiments. For instance, he regards the observations as not sufficiently extended, and lays emphasis on the fact that the method employed was purely chemical, while clinical and medical reports, which would have been of immense value, were not prepared. He criticises, also, the form of administration of the boron compounds, which certainly left something to be desired, and he does not consider that the hygienic arrangements were by any means satisfactory. There can be no doubt that a therapeutic test would have furnished more reliable data, and Dr. Liebreich appears to state his case with moderation, and to have estimated correctly the true value of the experiments and Dr. Wiley's report on them.

Foods and Food Control. U.S. Department of Agriculture, Bureau of Chemistry, Bulletin No. 69. Parts I. to VIII. By W. D. BIGELOW. Washington: Government Printing Office. 1905.

This compilation of the laws relating to food products, arranged under the headings of the various States, will be found very valuable by manufacturers and dealers who now experience some difficulty in keeping themselves informed of the exact details of the law as regards these substances, on account of the lack of uniformity in the different States and the constant alterations of the regulations. Consumers may also find the compilation useful, and it will be much appreciated by food inspectors. The first edition of the Bulletin was issued in 1902, since which date many legislative changes have been made, so much so that Dr. Wiley, the Chief of the Bureau of Chemistry, considered it advisable to revise the entire Bulletin, instead of merely printing the new laws and amendments, so that these five volumes give a complete review of all the laws now in force in each State, besides the Federal laws.

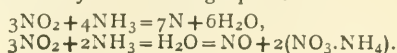
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

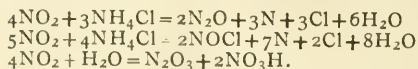
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 11, March 12, 1906.

Action of Hot Sulphuric Acid on Platinum and Iridium Salts in presence of Ammonium Sulphate.—Marcel Delépine.—The author isolates three species of irido-sulphuric salts, all strongly coloured. 1. Greenish blue salts which give a blue precipitate with salts of barium and strontium, and are decomposed by cold ammonia solution, giving a violet colouration. 2. Green salts which are not precipitated by neutral barium chloride, but can be precipitated to a greenish brown colour in an alkaline medium. The precipitate re-dissolves in acids, the green colour returning. These green salts also give with ammonia an olive-brown solution, which in time becomes greener, and is not precipitated by barium chloride, even when alkaline. 3. Olive brown salts which are not precipitated by neutral barium chloride, but give a brown precipitate in presence of ammonia. The solution darkens a little on the addition of alkalis. In all these bodies the sulphuric acid is apparently masked.

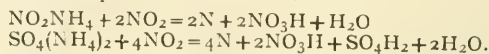
Action of Nitrogen Peroxide on Ammonia and certain Ammoniacal Salts.—MM. Besson and Rossel.—The principal reactions of ammonia gas on nitrogen peroxide under the conditions described by the author can be represented by the following equations:—



When the peroxide acts on ammonium chloride, the reactions are as follows:—



The peroxide of nitrogen acts on the nitrate and sulphate of ammonia under the same conditions as the chloride, but the gas evolved is exclusively nitrogen. The liquefied mass forms two superposed layers, of which the upper is formed of excess of peroxide; after elimination by distillation, in the first case nitric acid remains, and a mixture of nitric and sulphuric in the second:—



Action of Silicon Chloride on Cobalt.—Em. Vigouroux.—At a high temperature silicon chloride is reduced by cobalt, with formation of metallic chloride (which volatilises) and cobalt silicon (which remains). At about 1200–1300° the action ceases—that is to say, when the saturation is completed, and when the alloy contains about 19 to 20 per cent of combined silicon. This limit of silicification corresponds to the formula Co_2Si .

Dilactide of Lævo-lactic Acid.—E. Jungfleisch and M. Godchot.—In a previous research the authors described the preparation of the dilactide formed from dextro-lactic acid. They now prepare the corresponding compound produced from lævo-lactic acid. After purifications by crystallisation from ether, the *l*-dilactide forms crystals similar in appearance to those of the *d*-dilactide. The two dilactides combine to form (*d*+*l*) dilactide. This is much less soluble in ether than the active components. Combination easily takes place by separately dissolving equal quantities of the components in cold ether and mixing the two. Crystals of (*d*+*l*) dilactide are deposited.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Microscopical, 8. Exhibition of Lantern Slides of Plant Structure, prepared by A. Flatters.

CITY AND COUNTY OF BRISTOL.

PUBLIC ANALYST'S DEPT.—18, PRINCE STREET.

THE CORPORATION OF BRISTOL will shortly require the services of an ASSISTANT in connection with the work of the above Department.

The salary will be £91 per annum, and the candidate must possess Analytical experience.

Applications, endorsed "Assistant to Public Analyst," and accompanied by copies of three recent testimonials, must be sent to the undersigned at the Council House, Bristol, not later than the 23rd APRIL, 1906.

Dated this 4th day of April, 1906.

EDMUND J. TAYLOR, Town Clerk.

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THE WHEAT PROBLEM:

Based on Remarks made in the Presidential Address to the British Association at Bristol in 1898.

REVISED WITH AN ANSWER TO VARIOUS CRITICIS.

By SIR WILLIAM CROOKES, F.R.S.

With Two Chapters on the Future Wheat Supply of the United States, by MR. C. WOOD DAVIS, of Peotone, Kansas, and the HON. JOHN HYDE, Chief Statistician to the Department of Agriculture, Washington.

SECOND EDITION.

WITH PREFACE AND ADDITIONAL CHAPTER, BRINGING THE STATISTICAL INFORMATION UP TO DATE.

CHEMICAL NEWS OFFICE,
16, NEWCASTLE ST., FARRINGDON ST., E.C.

THE CHEMICAL NEWS.

VOL. XCIII., No. 2421.

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

PART II.—ANALYSIS OF THE TUNGSTEN GROUP.

By ARTHUR A. NOYES.

Introduction.

THE work upon the separation and detection of the elements whose hydroxides after heating at 120° are undissolved by nitric acid, constituting what for brevity is here designated the tungsten group,† has now been completed; but the method of procedure is still subject to revision as a result of information that may be gained in working out more fully the later groups, and additional test analyses covering other combinations of elements will be made as opportunity occurs. This publication is therefore to a certain extent a preliminary one.

The plan of presentation adopted in Part I. has been adhered to, special chapters being devoted to a "Tabular Outline" of the process, to a "General Discussion" of its main features, to the detailed "Procedure and Notes," to "Test Analyses" showing the efficiency of the method, and to "Confirmatory Experiments and References," substantiating the statements made in the notes.

I desire to state that during the first part of the work connected with this group Mr. B. E. Schlesinger was associated with me, and that to him are due the working out of the main sub-divisions of the group, and the discovery of the method of detecting tantalum in the presence of titanium. In the latter part of the work, consisting in perfecting the scheme and especially in developing the means of detecting niobium, tungsten, and tin, I have been ably assisted by Mr. D. P. Smith, and Mr. C. S. Bryan, jun. I also wish to express my thanks to Mr. F. M. Eaton for the valuable aid he has rendered by making a large number of test analyses by the final procedure.

Tabular Outline.

An outline of the process finally adopted is given in the table. Enclosure in brackets shows that the element may divide itself between the precipitate and filtrate at the point indicated.

General Discussion.

1. The residue insoluble in dilute nitric acid ordinarily contains all the tin, tungsten, tantalum, and niobium present in the substance, almost all of the antimony and titanium when these are present in even rather small quantities, much of the molybdenum and germanium when the substance contains a large quantity of them, and a greater or less proportion of many other elements, such as phosphorus, vanadium, arsenic, bismuth, selenium, tellurium, copper, iron, zirconium, which are carried down with the first-named elements. (See P. 5, N. 1, 3, 4, 5). Aside from the complications introduced by the occasional presence of these foreign elements, the difficulties involved in the separation, even sufficiently for qualitative purposes, of some of the regular elements of the group—especially of titanium, niobium, tantalum, and tungsten—have proved to be far greater than that of any other elements excepting the rare earths. And in spite of the existence of many analyses purporting to show the percentage composition of minerals containing two or more of these elements, it seems very doubtful whether any analytical method of separation has yet been developed by which quantitative results accurate even with in several per cent can be obtained. The

* From the *Technology Quarterly*, xvii., No. 3.

† Called the "niobium and tungsten groups" in Part I.

Tabular Outline.

<i>Residue</i> (SiO ₂ , TiO ₂ , Ta ₂ O ₅ , Nb ₂ O ₅ , Sb ₂ O ₅ , [Bi ₂ O ₃], SnO ₂ , [As ₂ O ₃], WO ₃ , [MoO ₃], &c.).—Dissolve in HF, pass in H ₂ S, and filter. (P. 31).			Distillate. SiF ₄ .
<i>Precipitate</i> ([Sb ₂ S ₅], [MoS ₃], [As ₂ S ₅], Bi ₂ S ₃ , &c.).—Boil with NHO ₃ and filter. (P. 32).			
<i>Residue</i> . [H ₂ MoO ₄], [H ₂ SbO ₄], Bi[N(O ₃) ₃], H ₃ AsO ₄ . (P. 51).			
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properties of these elements are therefore well worthy of more thorough going investigation from this point of view. The reader must not therefore be surprised to find that the scheme here proposed for the qualitative analysis of this group is somewhat complicated, and that it is not always possible to detect by it quantities as small as 1 or 2 m.grms. of some of these elements, when a large quantity of some other element is present.

2. The elements of this group are at the start present in hydrofluoric acid solution, the oxides having been treated with this solvent (P. 5) to remove silica, and to separate them from any undecomposed portion of the original substance. As experiments showed that the regular elements of the group, except antimony and molybdenum, are entirely unprecipitated by hydrogen sulphide from such a solution, while some of the foreign elements, bismuth, copper, selenium, and tellurium, are completely thrown out by it, it is thought best to submit the solution first to the action of this reagent. By this operation any complications that might arise in the later procedures from the presence of these elements are at once eliminated. A large part of the arsenic, antimony, and molybdenum is also removed, and this may be added to the main nitric acid solution, thereby making it unnecessary to test for these elements later in this group. Moreover, this treatment prevents so much molybdenum from being retained with the titanium in the ammonium sulphide precipitate, which otherwise is a rather serious difficulty when a very large quantity of this element is present. It is probable that this method, involving the use of hydrogen sulphide in hydrofluoric acid solution can be advantageously employed also for the quantitative separation of tin and tungsten from many of the other elements ordinarily precipitated by that reagent; it is not, however, possible in this way to separate those elements from antimony, arsenic, or molybdenum, since these are not by any means completely precipitated in the presence of hydrofluoric acid. The investigation of such quantitative methods can not be included within the scope of this research; but reference will occasionally be made to those which seem promising, in the hope that their study may be undertaken by others.

3. The solution is next evaporated with sulphuric acid to remove the hydrofluoric acid and decompose any fluosilicic acid. Sulphuric acid is used rather than nitric or hydrochloric, since it holds in solution, even after dilution, moderate quantities of all the elements of these groups except tungsten. Experiments were made in the hope of accomplishing the separation and detection of tungsten at this point; but, although when present alone 2 m.grms. give rise to a precipitate when the diluted sulphuric acid solution is allowed to stand, yet in the presence of titanium a much larger quantity remains in solution.

4. The method that naturally suggests itself for the subdivision of this group is digestion with ammonium sulphide solution, or fusion with sodium carbonate and sulphur followed by treatment with water, whereby titanium, niobium, and tantalum might be expected to remain undissolved, and tin, antimony, arsenic, tungsten, and molybdenum to pass into solution. This method is, in fact, often employed for the separation of titanium from tin and tungsten. Our experiments, like those of some previous investigators, have shown, however, that a considerable quantity of tungsten is retained in the titanium hydroxide precipitate, and that even 5 m.grms. of it may be removed so completely from the sulphide solution that it cannot be detected in the filtrate. Nevertheless, we have found no better method of separation than this, and have therefore made it an important part of the scheme of analysis for this group. This is further justified by the fact that the presence of tungsten in the titanium precipitate is indicated in the subsequent procedures, and that then it can, to a large extent, be separated from the titanium by fusion with sodium carbonate and sulphur, and be subsequently detected. The separation of tin from titanium by ammonium sulphide seems to be more satisfactory. Experiments on the method used by Defacqz for the separation

of titanium and tungsten, consisting in fusion of the oxides with a mixture of potassium nitrate and carbonate, did not give so satisfactory results.

5. The quantitative separation in the wet way of the three elements, titanium, niobium, and tantalum, present in the ammonium sulphide precipitate, is also, we believe, still an unsolved problem, and even the qualitative detection of small quantities of niobium and tantalum in the presence of much titanium presented so many difficulties that it was for a long time feared that the attempt to accomplish it would have to be abandoned. The method usually employed for the separation of niobium from tantalum, based upon the different solubilities of the potassium fluoxyniobate and fluoxytantalate, gives satisfactory results; but experiments showed that this method of conversion into double fluorides was not available for the separation of either of these elements from a large quantity of titanium, owing to the intermediate solubility of the potassium fluotitanate. The common quantitative method of separating titanium from the other two elements, by fusing the oxides with potassium disulphate and extracting with cold water the titanium sulphate, while leaving tantalum and niobium oxides undissolved, was found to be useless, since fairly large quantities of these elements also pass into solution when much titanium is present. Failure also attended attempts to separate these elements by treating their dried hydroxides with acidified hydrogen peroxide, and also by dropping an acid peroxide solution of them into a strongly ammoniacal solution of hydrogen peroxide, according to the method used by Walker for the separation of iron and titanium.

6. It was fortunately discovered, however, that an acid solution of hydrogen peroxide dissolves even large quantities of the precipitated hydroxides of niobium and titanium readily, and nearly completely, at any rate upon a repetition of the precipitation and treatment with peroxide; but that tantalum hydroxide, whether present in small or large quantity, whether alone or with much titanium, remains in large part (about one-half) undissolved by this solvent. It can therefore be detected in the residue by conversion into the insoluble potassium fluoxytantalate. The dissolved part does not, moreover, interfere with the tests adopted for the other two elements.

7. It then remained to devise a plan for the detection of titanium and niobium. No satisfactory method of separation could be found. It was proved, indeed, when the hydrogen peroxide was reduced by sulphurous acid and the solution made alkaline by ammonium hydroxide, that the precipitated hydroxide of titanium dissolved completely on strongly acidifying the solution with hydrochloric acid, while that of niobium, when present alone, remained in large part undissolved. But when much titanium was present with the niobium, considerable quantities of the latter went completely into solution, so that the method was unsuitable.

8. The attempt to effect a separation of the two elements was then given up, and characteristic reactions which would show one in the presence of the other were sought for. The yellow colour imparted to the peroxide solution is sufficiently characteristic of titanium, as neither tantalum nor niobium gives any colour to it. There seems to exist, however, no colour reaction given by niobium with a reagent which does not affect titanium. The idea then presented itself that the lower oxides, which are produced in the case of both elements by the action of zinc on acid solutions of the ordinary hydroxides, might possess markedly different reducing powers. This was found to be the case, for the lower oxide of titanium reduces mercuric chloride only very slowly, while that of niobium causes instantaneous reduction. Unfortunately, tungsten and molybdenum show the same behaviour as niobium, and they are apt to be retained in the ammonium sulphide precipitate; but it was found possible to remove them almost completely by the fusion with sodium carbonate and sulphur above referred to, so that error from this source may be avoided. It seems probable that the power of the

lower oxide of niobium of reducing mercuric chloride might be used for the quantitative estimation of this element in the presence of tantalum and titanium perhaps best by weighing the precipitated mercurous chloride.

9. Difficulty was also met with in the isolation of the tungsten from the alkaline sulphide solution; for upon acidification a large part, or if it is present in small quantity, almost the whole of that element, remains in solution, probably in a colloidal condition. Much more tungsten is precipitated if ferric chloride is added to the acidified solution, and the mixture is shaken and allowed to stand; but to detect small quantities of tungsten, it is even then necessary to recover it from the filtrate, so that the use of ferric chloride is not ordinarily to be recommended. The filtrate is merely evaporated, the residue ignited and fused with sodium carbonate, and the aqueous solution of it immediately tested for tungsten by acidification; so that no complications other than are involved in the performance of a few additional operations are introduced.

10. The sulphide precipitate may contain tin, antimony, tungsten, molybdenum, arsenic, and vanadium. It was found that the separation of the first two elements from any of the others (except molybdenum) by heating with concentrated hydrochloric acid was very imperfect, owing to the not inconsiderable solubility of the moist sulphides of tungsten, vanadium, and arsenic in that solvent. Fairly large quantities of tungsten especially went into solution when accompanied by a large quantity of tin, and thus escaped detection. On the other hand, the process sometimes used for the quantitative separation of tin and tungsten, which consists in igniting the sulphides in a current of hydrogen sulphide, and then treating them with strong hydrochloric acid, was found to give excellent results with all the metals concerned, and was adopted as part of the procedure. Incidentally it has the advantage of volatilising any arsenic present, which might otherwise prevent the separation of even a large quantity of tungstic acid in the later treatment of the sulphides with nitric acid.

11. The only other matter which requires mention is the separation of tungsten and molybdenum. When the latter element is absent, or present only in small quantity, tungstic acid alone separates as a yellow powder, upon treating with nitric acid the sulphides from which the antimony and tin have been previously extracted with hydrochloric acid; but if much molybdenum is present, even a considerable quantity of tungsten remains in solution, and if the solution is evaporated the molybdenum itself separates, after which it re-dissolves in acid with great difficulty. Some supplementary method of separation is therefore necessary. The most suitable one found is that of Ruegenberg and Smith as modified by Hommel, which consists merely in evaporating with sulphuric acid nearly to the fuming point, digesting for a time, and then diluting, whereby the tungsten is precipitated and the molybdenum retained in solution. The separation is not very sharp; yet as little as 3 m.grms. of tungsten always precipitate, while even a large quantity of molybdenum does not do so.

(To be continued).

Royal Institution.—On Tuesday next, April 24, at 5 o'clock, Prof. G. Baldwin Brown will commence a course of two lectures at the Royal Institution on "Greek Classical Dress in Life and in Art"; on Thursday, April 26, at the same hour, Dr. P. Chalmers Mitchell will deliver the first of two lectures on "The Digestive Tract in Birds and Mammals"; and on Saturday, April 28, at 3 o'clock, Prof. Charles Waldstein begins a course of three lectures on "English Furniture in the Eighteenth Century." The Friday Evening Discourses will be resumed on April 27, when Prof. J. W. Gregory will deliver a discourse on "Ore Deposits and their Distribution in Depth." The discourse on May 4 will be given by the Hon. C. A. Parsons on "The Steam Turbine on Land and at Sea," and on May 11 by Prof. J. P. Poynting on "Some Astronomical Consequences of the Pressure of Light."

A REVISION OF THE ATOMIC WEIGHTS OF SODIUM AND CHLORINE.*

By THEODORE WILLIAM RICHARDS
and
ROGER CLARK WELLS.

(Continued from p. 177).

PREPARATION OF PURE MATERIALS.

Water.

THE traces of organic impurity in the distilled water of the laboratory were eliminated by re-distilling from a weakly alkaline solution of potassic permanganate, using at first a glass condenser, and rejecting the first quarter of the distillate. Water thus prepared was pure enough for preliminary nephelometric work, when the presence of a trace of alkali could do no harm; it was usually kept in Jena flasks. In cases where the greatest purity was desired it was distilled, of course, once further, and for the nephelometric experiments it was kept in a closed bottle provided with a syphon and protected from possible traces of hydrochloric acid by a tube containing sodic hydroxide. For final preparations and accurate analyses, where silica and alkali must be excluded, the water was condensed and collected during the third distillation wholly in platinum. Care was taken to exclude dust in all stages of the proceedings; for, although visible dust might weigh little, its presence in silver halogen salt would produce decomposition and loss of weight in the final fusion. Only one who has attempted to exclude all dust from solutions can appreciate the difficulty of doing so. Thorpe and Roger (*Phil. Trans.*, 1894, A, clxxxv., 432), working upon viscosities, found that sealed-in condensers were very helpful in excluding dust from their distillates. We did not go as far as this, but the danger was borne in mind at every stage of the work and guarded against.

Hydrochloric Acid.

For the final work the purest acid of commerce was treated with a few crystals of potassic permanganate, diluted, and boiled. This should have expelled bromine and iodine, and must have oxidised any trace of organic matter which might have been present. The oxidation and boiling were repeated; the solution was fractionally distilled; and for the succeeding treatment the middle fraction was selected and subjected to another distillation, in which a platinum condenser and receiver were employed. As a matter of fact, most of these precautions were found to be unnecessary, since salt made, as described under "Sodic Chloride," from the best "chemically" pure acid of commerce only once re-distilled in platinum, without any further precautions, gave the same results as the purest material.

Sodic Chloride.

In most cases a perfectly pure salt cannot be made by precipitating the impurities, as many are prone to assume, but must itself be precipitated or crystallised from the less pure solution. Sodic chloride is nearly insoluble in a concentrated solution of hydrochloric acid; therefore the usual method of precipitation by means of hydrochloric gas seemed the best possible method of obtaining pure sodic chloride, since any included hydrochloric acid could be completely expelled by fusion. This expectation was confirmed by trial, and when it had been found that this means of purification was unusually suitable, most of the specimens of salt were treated in this way. This and other purifications were greatly assisted by centrifugal draining of the crystals. For this purpose salt was collected in a platinum funnel, and this was covered and supported on a stout frame capable of being whirled by means of strong cord about a radius of a metre. A test-tube, firmly fixed in the frame, collected the separated mother-liquor. Centrifugal draining, so important in technical work, has hardly received the attention which it

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deserves in the scientific laboratory. Experiments have shown that a good centrifugal apparatus is capable of separating nine-tenths or more, according to the habit of the crystals, of the mother-liquor which would otherwise contaminate the solid; hence making the purification at least ten times as effective as it would otherwise be (Richards, *Journ. Am. Chem. Soc.*, 1905, xxvii., 104). The whole treatment of precipitation and draining was carried on in platinum vessels which had been effectively freed from superficial iron.

Besides this chief mode of purification, others were used in special cases, and the original material came from a variety of sources, as recorded below. One of these was Merck's purest sodic chloride, which this firm stated had been prepared from German rock salt. Another was the very pure sodic sulphate prepared for the experiments on the transition temperature of this substance, and known to be very pure, because of the constancy and accuracy of its transition point (32.383°) (Richards and Wells, *Proc. Am. Acad.*, 1902, xxxviii., 431; also *Zeit. Phys. Chem.*, 1903, xliii., 465). Another was a fine specimen of Stassfurt halite, perfectly clear and colourless. A fourth specimen was made from the purest sodic bicarbonate manufactured by the Solvay Process Company, of Syracuse, New York, and very kindly furnished in large quantity by that company. A fifth sample was made from pure sodic carbonate from Merck. These preparations, differing widely in the steps of manufacture, and in geographical source, all yielded essentially the same atomic weight.

The source of the materials having been given above, it remains to record the details of their preparation.

In the first place, a large quantity of Merck's sodic chloride, which had been purified from German rock salt, was thrice re-precipitated by hydrochloric acid. This salt is designated "sample A" below, and was used in preliminary experiments. It was further crystallised from water (B); some of this was fused with ammonic chloride and ammonic chlorplatinate (C); a portion was then precipitated with hydrochloric acid (D); and finally some was again fractionated from water (E). None of these operations seemed to have any essential effect upon the combining weight of the salt; hence, even sample A must have been practically pure.

The very pure sodic sulphate was easily converted into chloride by successive precipitation from solution by means of gaseous hydrochloric acid. The sulphate forms an especially fortunate source of pure sodium, since none of the other alkaline sulphates yield crystals of the same degree of hydration or the same crystal form. Hence sodic sulphate which has been many times re-crystallised must be extremely pure. The ease with which a constant transition temperature may be obtained is evidence of this.

A specimen of sodic sulphate, which had been shown to be pure by its transition temperature, was twice further re-crystallised before adding hydrochloric acid. Four precipitations by this gas, with washings and drainings, removed practically all of the sulphuric acid. Nevertheless, when the mother-liquor was concentrated by evaporation and tested, an extremely small trace of sulphate was found by excess of baric salt to persist until the tenth precipitation. There was no trace of visible baric sulphate on testing the mother-liquor, even in the nephelometer, after the eleventh precipitation, but the salt was precipitated once more for certainty. This salt, thus twelve times separated by hydrochloric acid, was designated F. It seems highly probable that since so large an amount of sulphuric acid was eliminated from it by this treatment, all other impurities must have been separated.

For another specimen of salt, a number of fine, large, colourless transparent crystals of halite, from near Stassfurt, Germany, were dissolved in pure water. After the addition of a little sodic hydroxide, boiling, and standing, the solution was filtered and precipitated with hydrochloric gas. A solution of the latter salt in water stood several days. The clear decanted portion was precipitated twice more, fractionally crystallised from

water, and dried over sodic hydroxide in a vacuum desiccator. This specimen was called sample G.

The bicarbonate from Syracuse, New York, was of the following composition, according to the report of the Solvay Process Company:—

	Per cent.
Silica	0.006
Ferric oxide and alumina	0.002
Calcic carbonate	0.030
Magnesian carbonate	0.005
Sodic chloride	0.070
Sodic carbonate	0.522
Sodic bicarbonate	99.300

This material, already very pure for a commercial substance, was easily further purified by repeated washing with cold water, which was sufficient to remove most of the chloride.

A portion of the Syracuse bicarbonate, thus washed four times with cold water and thoroughly drained each time with a reverse platinum filter, was nearly all dissolved in water. After settling, the resulting clear solution was decanted, neutralised with hydrochloric acid, and then evaporated to dryness. The sodic chloride was fused in platinum, dissolved, and considerably diluted. After long standing the clear upper portion was decanted from very finely divided silica. This method of fusion is a very effective means of separating silica, but the precipitate is so fine as to require a long time to settle, and has to run through most filtering septa. Hence, cautious decanting, with rejection of the considerable lower portion of the solution, is necessary. The unimpeachable solution of salt thus obtained was concentrated and twice precipitated by hydrochloric gas (H), twice more precipitated (I), and yet twice more precipitated (J). Analysis showed these three to be alike, as will be recorded.

The Merck bicarbonate was thoroughly washed and once re-crystallised from water. It was then gently ignited, and the normal carbonate was three times crystallised from water. From this carbonate, by the usual process of precipitation by hydrochloric gas and crystallisation from water, sample K was prepared. This sample gave essentially the same combining number as the others.

With such conclusive evidence that no foreign base was present, we turned our attention to the acid. The preceding preparations had all been precipitated with hydrochloric acid gas, obtained simply by warming the highly concentrated purest acid of commerce, because we deemed it more convenient to use this constant material, even if slightly impure, than to prepare so large a quantity of the purest acid. A special set of comparative experiments, made with the purest acid, proved that the other material had, as a matter of fact, been pure enough for the most exacting requirements.

For this purpose the very pure hydrochloric acid was used whose preparation is described above. This acid was neutralised by an especially prepared sample of soda, made from a second portion of the Syracuse bicarbonate. The purification was conducted wholly in platinum vessels, of course. After being washed as before, the bicarbonate was dried and heated, to convert it into the normal carbonate. The solution of the latter in water was decanted daily as long as long as any precipitated residue (calcic carbonate) appeared visible. The sodic carbonate was then re-crystallised four times, as the deka- or hepta-hydrate, and once as the anhydrous salt. A concentrated solution of the latter salt was then treated for a considerable time with carbon dioxide under a bell-jar until the bicarbonate had formed. The carbon dioxide was made by gently heating sodic bicarbonate, and was well washed with pure water. The pure bicarbonate thus formed was washed with cold water, thoroughly drained, and dissolved in an excess of the pure hydrochloric acid. The resulting salt was twice fractionally re-crystallised from water on the steam bath; and the crystals were washed and drained each time, in order to free them from any possible calcium or magnesium chlorides, which are not easily eliminated from carbonate,

Since the atomic weight from this preparation (L) was identical with that from the preceding preparations, the previous salts, made by precipitation with hydrochloric gas, could have contained no other halogen than chlorine.

It appears from the identity of all these specimens that sodic chloride is among the substances whose preparation in a pure state is an easy problem. It is further true that the expulsion of water from it upon fusion without loss of halogen is a very simple matter; moreover, since we succeeded in proving that salt fused in a vacuum possesses the same combining weight as that fused in air, the solid contains neither occluded oxygen nor nitrogen in weighable amounts. This matter is discussed later on.

Considering these experiments, it is fairly safe to infer that all the various preparations of sodic chloride were quite free from significant quantities of any foreign substance.

(To be continued).

THIRTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1905.*

By F. W. CLARKE.

(Continued from p. 171).

Bromine.

In his research upon the atomic weight of iodine, Baxter (*Journ. Am. Chem. Soc.*, xxvii., 884) made a series of experiments upon the conversion of silver bromide into chloride by heating in a current of dry chlorine. Vacuum weights are given in the following table, and reduced with $Ag = 107.93$ and $Cl = 35.473$.

Weight AgBr.	Weight AgCl.	Atomic weight Br.
10.92091	8.33538	79.955
13.88062	10.59457	79.951
8.21484	6.27006	79.952
7.87887	6.01352	79.956
6.90106	5.26735	79.951
9.53704	7.27926	79.952
Mean		79.953

This is sensibly identical with the generally accepted value, 79.955.

Iodine.

An important continuation of the research upon iodine, which was reported in 1904, has been published by Baxter (*Journ. Am. Chem. Soc.*, xxvii., 876). First, silver iodide was converted into bromide by heating in bromine. The corrected data are as follows:—

Weight AgI.	Weight AgBr.	Atomic weight I.
13.65457	10.92091	126.985
17.35528	13.88062	126.987
9.70100	7.75896	126.982
10.27105	8.21484	126.983
9.85688	7.88351	126.986
8.62870	6.90106	126.991
11.92405	9.53704	126.981
7.56933	6.05389	126.987
Mean		126.985

Atomic weights calculated with $Ag = 107.93$, $Br = 79.955$.

Two new series of determinations were made of the ratio $AgI : AgCl$. The first of these was upon the weights of iodine given in the foregoing table; that is, the bromide, after weighing, was transformed into chloride.

Weight AgI.	Weight AgCl.	Atomic weight I.
Series II.		
13.65457	8.33538	126.985
17.35528	10.59457	126.983
10.27105	6.27006	126.980
8.62870	5.26735	126.985
11.92405	7.27926	126.976
Mean		126.982
Series III.		
9.26860	5.65787	126.990
6.72061	4.10259	126.984
11.31825	6.90912	126.987
10.07029	6.14754	126.979
13.49229	8.23649	126.980
Mean		126.984

Three additional series of measurements relate to the ratio between silver and iodine. In the first one, iodine and silver were weighed separately; the iodine was then converted into hydriodic acid and precipitated by known quantities of silver.

Weight I.	Weight Ag.	Atomic weight I.
3.29308	2.79897	126.983
3.70132	3.14584	126.988
3.75641	3.19258	126.991
3.24954	2.76186	126.988
4.12541	3.50639	126.984
3.53166	3.00165	126.988
2.99835	2.54842	126.985
2.00015	1.69991	126.993
Mean		126.987

In five of these experiments the silver iodide was collected and weighed, with the subjoined results.

Weight I.	Weight AgI.	Atomic weight I.
3.75641	6.94913	126.987
3.24954	6.01137	126.989
4.12541	7.63204	126.977
3.53166	6.53351	126.979
2.99835	5.54682	126.983
Mean		126.983

Finally, in order to determine the ratio $Ag : AgI$, the filtrate and washings from the previous sets of analyses were examined for the silver they might contain. This gave a small correction to the weights already cited, with results as follows:—

Weight Ag.	Weight AgI.	Atomic weight I.
3.19249	6.94877	126.990
2.76175	6.01110	126.986
3.00189	6.53399	126.993
2.54833	5.54659	126.986
Mean		126.989

The final value adopted by Baxter is $I = 126.985$ when $Ag = 107.93$ and $Cl = 35.473$. Vacuum weights are given throughout the memoir. Two short critical papers on iodine, by Ladenburg (*Ann.*, cccxxxviii., 259) and Koethner (*Ann.*, cccxxxviii., 262) respectively, have also appeared during the year. They contain no new determinations.

Sodium.

The determinations of the atomic weight of sodium by Richards and Wells cover the measurement of two ratios (*Journ. Am. Chem. Soc.*, xxvii., 459; *CHEMICAL NEWS*, xciii., p. 175; original in Publication 28 of the Carnegie Institution). It goes without saying that in all of Richards' work every conceivable precaution is taken and every cor-

* From the *Journal of the American Chemical Society*, xxvii., No. 3.

rection applied. The data obtained appear in the two following tables:—

Ratio NaCl : AgCl.		
Weight NaCl.	Weight AgCl.	Ratio, 100 AgCl : NaCl.
3·27527	8·03143	40·781
5·56875	13·65609	40·779
4·18052	10·25176	40·779
4·54319	11·14095	40·779
1·97447	4·84190	40·778
3·97442	9·74547	40·782
6·69495	16·41725	40·780
2·88692	7·07955	40·778
5·56991	13·65833	40·780
5·85900	14·36693	40·781
Mean		40·780

Ratio Ag : NaCl.		
Weight NaCl.	Weight Ag.	Ratio, 100 Ag : NaCl.
3·96051	7·30896	54·187
2·32651	4·29355	54·186
5·36802	9·90699	54·184
4·00548	7·39210	54·186
4·69304	8·66101	54·186
3·27189	6·03842	54·185
5·08685	9·38795	54·185
3·66793	6·76952	54·183
5·48890	10·12993	54·185
3·55943	6·56909	54·185
Mean		54·185

Two supplementary analyses for fixing the foregoing ratio were made with salt and silver which had both been fused *in vacuo*.

NaCl.	Ag.	Ratio.
3·38684	6·25046	54·185
4·68529	8·64634	54·188

With Ag = 107·92 and Cl = 35·470 we have for Na, from AgCl ratio, Na = 23·004; from Ag ratio, Na = 23·007. With Ag = 107·93 and Cl = 35·473, Na = 23·008.

Potassium.

Atomic weight re-determined by Archibald from analyses of the chloride (*Trans. Roy. Soc. Canada*, 1904, Section III., p. 47). Two ratios were measured. The data given below represent vacuum weights.

Ratio AgCl : KCl.		
Weight AgCl.	Weight KCl.	Ratio.
4·25916	2·21586	52·028
3·83250	1·99379	52·023
5·57396	2·89977	52·025
9·10362	4·73606	52·026

Ratio Ag : KCl.		
Weight Ag.	Weight KCl.	Ratio.
3·20598	2·21586	69·116
2·88479	1·99379	69·114
4·19557	2·89977	69·115
6·85280	4·73606	69·111

In mean K = 39·140 when Ag = 107·93 and Cl = 35·455. With Cl = 35·473, this becomes K = 39·122.

Carbon and Glucinum.

Parsons (*Journ. Am. Chem. Soc.*, xxvii., 1204) has discussed his analyses of the basic acetate and acetyl-acetate of glucinum, which were noticed in the report for 1904. Combining the two equations yielded by the two observed ratios, and solving algebraically, the following values were simultaneously determined:—

$$\text{Gl} = 9·112 \quad \text{C} = 12·007.$$

From the density and critical constants of CO₂, Guye (*Comptes Rendus*, cxli., 1241) finds C = 12·003; and from C₂H₂, C = 12·002. Jaquero and Perrot (*Comptes Rendus*, cxli., 1542), by comparing the densities of gases at 1067°₀, find the molecular weight of CO to be 28·009, and of CO₂ 43·992. Hence C = 12·009 and 11·992.

Guye and Pintza (*Comptes Rendus*, cxli., 51) have also determined anew the density of carbon dioxide. One litre at normal temperature and pressure weighs 1·97684, 1·97676, 1·97681 grms.

Lord Rayleigh (*Phil. Trans.*, cciv., 369), studying the compressibility of gases, has deduced several molecular weights from measurements of density at ordinary pressures and very small pressures. The subjoined data refer to carbon monoxide and dioxide when O₂ = 32.

	Atmospheric P.	Very small P.
Carbon monoxide ..	28·000	28·003
Carbon dioxide ..	44·268	44·014

From the figures in the second column, CO—O gives C = 12·003. CO₂—O₂ = 12·014, 2CO₂—CO = 11·992. From the density of hydrogen at very small pressures, H₂ = 2·0173.

(To be continued).

CONGRESS OF APPLIED CHEMISTRY AT ROME.

THE MORE IMPORTANT QUESTIONS TO BE DISCUSSED
AT THE SIXTH INTERNATIONAL CONGRESS.

THE Sixth International Congress of Applied Chemistry will be held at Rome from April 26th to May 3rd, under the distinguished patronage of His Majesty the King of Italy. The character of the Congress will be veritably international, for it has been supported by, and received many communications from, the chemists of England, France, Germany, Austria, Hungary, Belgium, Switzerland, Spain, Holland, Norway, Russia, Roumania, Greece, Tunis, Egypt, India, Cape Town, United States of America, Argentina, Brazil, Chili, and Uruguay, besides those of Italy.

The English Committee, which is composed of delegates of fifteen of the principal societies of chemistry and the allied sciences, has for its general hon. secretary C. G. Cresswell (Palace Chambers, Westminster, S.W.). We hear that a large party of English chemists will leave London on April 23rd, and, going by way of the Lake of Como, will join the Congress at Rome.

Among the more important communication which will be read before the Congress we may mention that of Sir William Ramsay, "Sur l'Epurage des Eaux d'Egoût"; that of Henri Moissan, of Paris, "Sur la Distillation des Metaux"; and that of A. Frank, of Berlin, "Sur l'Utilisation Directe de l'Azote de l'Atmosphère pour la Production des Engrais et de Produits Chimiques."

Among the more important communications from the English chemists we note the following:—"Acido Solfonico Fermentazioni," by Dr. W. Stevens, of London; "The Systematic Study of Absorption Spectra as Applied to Determining Problems of Chemical Constitution in Colourless and Coloured Substances;" "The Application of Photography to the Solution of Problems in Chemistry," by Prof. W. N. Hartley, of Dublin; "The Fight between Cane- and Beet-sugar," by Dr. S. Stein, of Liverpool; "The Most Recent Methods for the Electrolytic Refining of Copper," by Dr. S. Cowper Coles, of London; "On certain Cases of Hydrolysis," by Dr. V. H. Veley, of Oxford.

Also the following important communications from the American chemists:—"Fused Sodium Peroxide and its Use in Air Purification," by Prof. P. Herbert and R. Forreger, of New York; "Comparison of the Characters of Petroleum of Recent Development with that of the Older Sources of Supply," by Dr. R. Clifford, of New York;

"The Effect of Environment upon the Composition of Sugar-producing Plants; "Important Problems of Agricultural Chemistry in the United States"; "The Inspection of Food Products Imported into the United States"; "The Use of Sulphur Fumes in the Preparation of Food Products," by Dr. H. W. Wiley, of Washington; "Dry Lead Defecation in Optical Sugar Analysis," by Dr. W. Horne, of New York.

The chemists of India announce the following papers:—"A Comparative Study of the Chief Methods for Estimating the Quantity of the Various By-products of Spirituous Liquors, with Analyses"; "The Chemistry and Comparative Toxicity of the By-products (a) of Potable Spirits made in India, (b) of Spirits Imported into India from Europe," by Prof. C. H. Bedford, of Calcutta; "Analyses of Effluents of Septic Tanks for Sewage Disposal in India," by Dr. Leather, of Bombay; "The Toxic Principle in the Bitter Variety of *Luffa Ægyptiaca*," by Dr. C. L. Bose, of Calcutta.

We may also call attention to the following:—"Which are the Most Suitable Means for Retarding the Fermentation of Must in Hot Climates to Secure Wines of better Bouquet," by Prof. P. D. Hahn, of Cape Town; "On the Chemistry of the Lakes Employed in Dyeing," by Prof. Z. Pocopiens, of Athens; "The Chemical Selection of the Cane," by Dr. Kobus, of Pekalongan (Java).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 30th, 1906.

Professor R. MELDOLA, F.R.S., President, in the Chair.

PROF. J. J. SUDBOROUGH and Mr. J. L. BAKER were appointed Scrutators, and the Ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT presented the Report of the Council on the progress of the Society during the past twelve months. The adoption of the Report of the Council was proposed by Mr. R. J. FRISWELL, seconded by Dr. H. BRERETON BAKER, and carried unanimously.

Report of the Council.

The Council have the satisfaction of being able to report that the past year has been a prosperous one for the Society, the activity of which, as measured by the number of papers read and the number of Fellows on the list, has exceeded that of any previous year.

On the 31st December, 1904, the number of Fellows was 2711. During 1905, 164 Fellows were elected and 2 re-instated, thus making a gross total of 2877. The Society has lost 25 Fellows by death, 28 have resigned, the election of 3 has become void, 1 has withdrawn, and 35 have been removed for non-payment of Annual Subscriptions. The total number of Fellows, therefore, on the 31st December, 1905, was 2785, showing an increase of 74 over the number for the previous year.

The names of the deceased Fellows, with the dates of their election, are:—W. Ackroyd (1897), C. M. Blades (1885), J. F. Braga (1881), G. B. Buckton (1852), J. L. Bullock (1842), C. F. Burnard (1849), J. H. Calvert (1871), H. S. Carpenter (1875), J. Duncan (1863), H. S. Elworthy (1886), J. Epps (1885), E. Graham (1895), W. H. Greenwood (1873), F. W. Harrold (1891), F. M. Mercer (1884), M. Prasad (1903), A. B. Prescott (1876), W. T. Rickard (1845), R. Roose (1886), F. Shapley (1893), C. W. Sutton (1884), C. R. C. Tichborne (1863), L. White (1862), W. W. Will (1885), R. Yates (1874).

The small number of Fellows still living who were elected in the early days of the Society has been further reduced by the death of Mr. G. B. Buckton, who was elected in March, 1852, and of Mr. J. L. Bullock, elected in 1842. Since the close of 1905, the Society has had to

lament the loss of Professor Hermann Johann Philipp Sprengel, who was elected in December, 1864.

The number of Honorary and Foreign Members at the date of the last Annual General Meeting was 35. No names have been added to the list since then, but the Society has sustained a loss in the death of Professor P. T. Cleve, who was elected in February, 1883, and who died on June 18th, 1905. The work of the deceased Honorary and Foreign Member is to be commemorated by a Memorial Lecture, the delivery of which has been undertaken by Professor T. E. Thorpe.

During the year 1905, 233 scientific communications have been made to the Society, 191 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1905 contains 1936 pages, of which 1818 are occupied by 184 memoirs, the remaining 118 pages being devoted to the Wislicenus Memorial Lecture, the Obituary Notices, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 175 memoirs, which occupy 1715 pages.

The *Journal* for 1905 contains also 4356 abstracts of papers published mainly in foreign journals, which extend to 1828 pages, whilst the abstracts for 1904 numbered 4617 and occupied 1920 pages.

The abstracts for 1905 may be classified as follows:—

PART I.		Pages.	No. of Abstracts.
Organic Chemistry	956	1727	
PART II.			
General and Physical Chemistry ..		619	
Inorganic Chemistry		562	
Mineralogical Chemistry		71	
Physiological Chemistry		467	
Chemistry of Vegetable Physiology and Agriculture		295	
Analytical Chemistry		615	
	872	2629	
Total in Parts I. and II. ..	1828	4356	

In making comparison with the preceding year, it must be borne in mind that the 1904 volume contained the abstracts for thirteen months. Owing to the change in date of publication, no abstracts appeared between December 1st, 1903, and January 31st, 1904, so that the number of the *Journal* published on the latter date contained practically the abstracts of two months (see *Trans.*, 1905, lxxxvii., 539).

The Council regrets to announce that Dr. G. T. Morgan has found it necessary to resign the post of Editor of the Society's publications which he has occupied so creditably since the beginning of 1903. Although his resignation was received in September, 1905, Dr. Morgan kindly acted as Editor until the appointment of his successor, Dr. J. C. Cain.

The second part (Subject index) of the Collective Index for the decade 1893-1902 was issued in December, 1905, to those Fellows who had made application for it in accordance with the printed notices circulated with the monthly parts of the *Journal* subsequently to July, 1903, and the Council have pleasure in expressing the high appreciation of the ceaseless energy displayed by the Indexer, Mrs. Margaret Dougal, on the completion of this valuable work.

During the vacation of 1905, advantage was taken of the Doctorial Jubilee of Professor Adolph von Baeyer, and of the Professorial Jubilee of Professor Mendeléeff, to address letters of congratulation to these two distinguished Honorary and Foreign Members.

In June, 1905, the Council decided that the Ordinary Meetings of the Society should be held during the ensuing Session on the first and third Thursdays of the month at 8.30 p.m. The experiment of holding the meetings on

Wednesday afternoons at 5.30 p.m., alternately with Thursday evenings at 8 p.m., had been in operation since January, 1902, and from the fact that the average attendance of Fellows at the afternoon meetings had undergone steady diminution during this period, whilst the number of Fellows attending the evening meetings had increased, it has been concluded that a majority of the Fellows who make a practice of attending the meetings find the evening more convenient than the afternoon.

The Library has received an important addition by the generosity of Sir Henry E. Roscoe, who has presented to the Society a collection of 136 alchemical and early chemical works of great interest and value.

An increase in the use of the Library is recorded, 1108 books being borrowed during 1905, as against 1057 in the previous year. Additions to the Library, excluding Sir Henry Roscoe's donation, comprise 165 books, of which 58 were presented, 324 volumes of periodicals, and 48 pamphlets, as against 119 books, 296 volumes of periodicals, and 52 pamphlets last year. On the recommendation of the Library Committee the Council have made an addition to the Library Rules in the following terms:—"No persons other than Fellows of the Society have the privilege of using the Library, except upon a written introduction from a Fellow, with whom rests the responsibility for all books consulted by the person introduced. Such introduction shall be valid for one occasion only."

Grants amounting in all to £236 have been made during the year from the Research Fund, and £22 15s. 3d. has been returned. Of the papers published in the *Transactions* during 1905, 24 were contributed by authors to whom grants had been made from the Research Fund.

In February of last year the Treasurer was fortunate enough to be able to increase the invested capital of the Society by almost exactly £1500 by the purchase of £1983 Midland Railway 2½ per cent Preference Stock for £1499 14s. 5d. The income from all sources for the year 1905 exceeds that for 1904 by only £93 8s. 4d., whilst the expenditure has been abnormally heavy, exceeding the total income by £305 1s. 5d. This is due to the incidence of several very heavy accounts, one of which really belongs to several years, and that is the completion of the Decennial Index for the period 1893-1902, which has entailed the expenditure this year of no less than £778 10s. 5d., or rather more than half the total cost. No further expenditure, however, on account of Decennial Indexes will be required for several years to come. As pointed out last year, the continual increase in the cost of the *Journal* and *Proceedings* is a source of much anxiety, and this year a further increase has to be recorded on both accounts, £219 12s. 7d. in the former and £35 18s. 2d. in the latter case, or a net increase over the cost of both in 1904 of £255 10s. 9d., and over that in 1903 of £578 3s. 3d. The Council therefore trust that authors of papers will do their utmost to assist the Publication Committee and the Treasurer in keeping down the cost of printing as far as possible.

The publication of the *Annual Reports on the Progress of Chemistry* has necessarily added materially to the expenditure of the Society; the cost of Volume I. having entailed an expenditure of £445 19s. 6d., of which about £70 has been recovered by their sale. Another item of some magnitude, £52 9s. 6d., is the cost of the printing and circulating of the Bye-laws, together with the changes proposed by the Council, which were submitted to an Extraordinary General Meeting on February 8th, 1905.

The administrative expenses have been carefully kept in check, and whilst everything has been maintained in a state of thorough efficiency their amount is only £827 16s. 5d., as against £893 1s. 0d. in 1904.

The following facts with regard to the cost of the Decennial Indexes may be of interest. The total cost of Volume IV., 1893-1902 (Parts I. and II.), exclusive of distribution, amounts to £1454 5s. 6d., of which the cost of printing was £762 6s. 0d. The cost of Volume III., 1883-

1892 (issued in one volume) was £1280 2s. 7d., of which the printing accounted for £585 19s. 7d. The cost of Volume IV. was relatively considerably less than that of Volume III., as the former extended to 45½ sheets for the Authors' Index and 108 sheets for the Subject Index, or 153½ sheets in all, whilst Volume III. only contained 102½ sheets. Owing to the way in which the Annual Indexes are now prepared, it is hoped that when Volume V. has to be undertaken, the relative cost will be still further reduced and that the chief cost will be that due to the printing.

The Treasurer gave a statement as to the Society's income and expenditure during the year 1905, and proposed a vote of thanks to the Auditors, which was seconded by Dr. BERNARD DYER and carried unanimously, acknowledgment being made by Dr. H. FORSTER MORLEY.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Dr. T. E. THORPE, seconded by Sir THOMAS STEVENSON, and unanimously adopted. Sir WILLIAM RAMSAY responded.

The President then delivered his Address, entitled "The Living Organism as a Chemical Agency: A Review of some of the Problems of Photosynthesis by Growing Plants."

Sir HENRY E. ROSCOE proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the Society's *Transactions*. Dr. HORACE BROWN seconded the motion, which was carried by acclamation, and acknowledged by the President. (The Address will appear in the April number of the *Journal*.)

The Scrutators then presented their Report to the President, who declared the following to have been duly elected as Officers and Council for the ensuing year:—

President—Raphael Meldola, F.R.S.

Vice-Presidents who have filled the office of *President*—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; W. H. Perkin, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents—Horace T. Brown, LL.D., F.R.S.; Harold B. Dixon, M.A., F.R.S.; Rudolph Messel, Ph.D.; W. H. Perkin, jun., Ph.D., F.R.S.; A. Smithells, B.Sc., F.R.S.; W. P. Wynne, D.Sc., F.R.S.

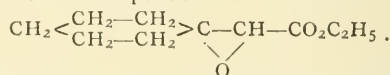
Treasurer—Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries—M. O. Forster, D.Sc., Ph.D., F.R.S.; A. W. Crossley, D.Sc., Ph.D.

Foreign Secretary—Sir William Ramsay, K.C.B., LL.D., F.R.S.

Ordinary Members of Council—Edward C. C. Baly; Bernard Dyer, D.Sc.; William Gowland; Alfred D. Hall, M.A.; H. A. D. Jowett, D.Sc.; A. Lapworth, D.Sc.; J. E. Marsh, M.A.; F. E. Matthews, Ph.D.; G. T. Moody, D.Sc.; A. G. Perkin, F.R.S.; W. J. Sell, M.A., F.R.S.; John Wade, D.Sc.

Preparation of Glycidic Ethers and Aldehydes of the Hexahydroaromatic Series.—Georges Darzens and P. Lefebure.—The authors prepare from cyclohexanone and monochloroacetic ether mixed with sodium ethylate, with a yield of 65 per cent, the ether of cyclohexylacetic oxide, which has composition—



To prepare the hexahydrobenzoic aldehyde, the free acid must be slowly distilled in a vacuum, when decomposition takes place, the aldehyde and CO₂ being formed.—*Comptes Rendus*, cxlii., No. 12.

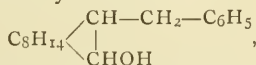
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 12, March 19, 1906.

Distillation of Titanium and the Temperature of the Sun.—Henri Moissan.—The author finds that though the boiling-point of titanium is very high this metal can be distilled regularly. The series of experiments on the distillation of metals and non-metals lead to very interesting conclusions regarding the temperature of the surface of the sun. It is found that the maximum temperature of the electric arc is about 3500°. At this temperature all known bodies are gaseous, which result seems to point to the fact that the temperature of the sun is not above 3500°. It must be remembered, however, that these experiments are made under atmospheric pressure, and the pressure is probably very different on the solar surface.

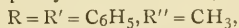
Benzyl and Phenylborneols and their Products of Dehydration, the Benzyl and Phenylcamphenes.—A. Haller and E. Bauer.—It is known that the borneols and iso-borneols give, on dehydration, camphenes which, when treated with formic or acetic acid or in presence of sulphuric acid, give rise to the ether salts of the iso-borneols. The authors now prepare the secondary benzylborneols and the tertiary benzyl and phenylborneols, as well as their products of dehydration, the benzyl and phenylcamphenes. The secondary benzylborneols are the reduction products of benzylcamphor, and are represented by the formula—



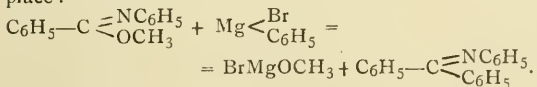
Action of Imino-ethers and Imino-chlorides on the Organo-magnesium Derivatives.—R. Marquis.—The synthesis of ketones by means of organo-magnesium derivatives has already been effected in different ways. The author solves the same problem by another method which is based on the following considerations:—The action of the ether salts on organo-magnesium derivatives gives tertiary alcohols. This reaction takes place in two phases. (a) Fixation of a molecule, $\text{R}-\text{Mg}-\text{X}$, on to the CO of the $-\text{CO}.\text{OR}'$ group. (b) A double exchange

between R and OR', resulting in the group $-\text{C} \begin{cases} \text{OMgX} \\ \text{R} \end{cases}$.

If the reaction is limited to the latter phase the group CO is blocked, and a ketone derivative results. The author therefore substitutes the imino-ethers $\text{R}-\text{C} \begin{cases} \text{NR}' \\ \text{OR}' \end{cases}$. He first uses methyl phenylimino-benzoate,—



with magnesium phenylbromide, when under the conditions described by the author the following reaction takes place:—



Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 4, 1906.

Crystalline Liquid Substances.—D. Vorländer.—*p*-Azoxy-benzoic acid ethyl ester is capable of existing in an anisotropic liquid phase. It has two sharp melting-points; the first, at which the solid crystalline form passes into the turbid anisotropic liquid form, occurs at 114°, and the second, at which the turbid liquid passes to the clear isotropic liquid, at 121°. Both transformations are sharp, and

occur quickly. The author has now discovered certain parallels between the azo- and azoxy-anisols, and the azo- and azoxy-benzoic acid esters. In both cases it is the azoxy-group which causes the crystalline liquid phase, for the phenomenon does not occur when they are reduced to the azo bodies. Moreover, the para-position of the substituent has an influence on the phenomenon, for *o*-azoxy-anisol forms no crystalline liquid, while the para-anisol does. The formation of the crystalline liquid is produced or favoured by the presence of the same atomic groups as those which influence other physical properties, the refraction of light, colour, rotatory power, &c. Thus all aliphatic esters of *p*-azoxy-cinnamic acid, from the methyl to the cetyl ester, have this property. Unlike the aliphatic esters, the benzyl ester of *p*-azoxy-cinnamic acid does not exhibit the phenomenon, but melts in the usual way, while the acetic acid residue and the acetophenone residue both give the anisotropic liquid and the two melting-points.

Nature of the so-called Metallic Ammonium Compounds.—Otto Ruff and Emil Geisel.—Lithium (+70°), sodium (-20°), potassium (a little above 0°), rubidium (-3°), cesium (+40°), calcium (+20°), strontium (+40°), and barium (temperature not known) at atmospheric pressure react with ammonia at the temperatures given in brackets. In the case of the alkali metals and strontium, the metal first becomes indigo-blue on its surface; the colour then rapidly changes to a beautiful metallic red (more yellowish with lithium), and then yields a solution which is an intense dark blue when very dilute. If the pressure of the ammonia above the solution is diminished, or the temperature raised, the solution loses ammonia, and coppered crystalline masses separate out. When all the liquid solution has disappeared, these masses lose ammonia, and the metal is left behind in the crystalline form. The phenomena of the crystallisation of these solutions resemble those of many saturated solutions. Calcium behaves slightly differently because it is only very slightly soluble in liquid ammonia. The authors have shown that the red masses, although their composition is represented by 1Me to 1NH₃, are not chemical compounds, but that they consist of metal and liquid saturated solution. To separate solid and liquid a centrifuge was used, which, however, only partially overcame the adhesion of the solution to the solid residue. However, by packing some of the metallic ammonium in a linen cloth at a low temperature and applying pressure, the solution could be forced through the cloth, and the metal left behind. This process was not successful in the case of the caesium-ammonium substance, because it contains only 0.17 gm. of ammonia to 1.33 gm. of caesium, and it is naturally difficult to squeeze out such a small amount of liquid. The residue on the cloth, in the case of sodium and potassium ammonium, consisted of a compact piece of metal, while lithium appeared finely powdered. Rubidium and caesium caught fire on the cloth. The saturated solutions contain at -80° 1Na to 5.2 NH₃, 1K to 4.81 NH₃, and 1Li to 3.93 NH₃. In the cases of potassium, sodium, and lithium, the solubilities were determined within as wide a temperature interval as possible, and it was proved that besides metal and saturated solution no other solid or liquid phase could ever be detected. The solution of the alkali metals in liquid ammonia, which proceeds with exceedingly slight development of heat, is not due to transpositions such as those which occur between sulphur and liquid ammonia, but the liquids obtained are undoubtedly true solutions. The solutions of metals in non-metallic solvents seem to constitute a special type, and to possess properties marking them out from ordinary solutions. Among these characteristic properties may be mentioned their colour and their behaviour towards the electric current.

Conversion of Oxygen into Ozone at a High Temperature, and the Oxidation of Nitrogen.—Franz Fischer and Fritz Braehmer.—The authors have come to the conclusion that in order to obtain ozone by heating oxygen, the heated gases must be cooled before the ozone

has time to decompose. To do this they tried the effect of heating by various means oxygen, also as liquid air and liquid oxygen. They first investigated the phenomenon of combustion in liquid air, burning hydrogen, carbon monoxide, acetylene, &c., thus employing a high temperature caused by heat of reaction; the result of these experiments was that in the filtrate from the liquid air ozone was always found, and nitrogen oxides upon the filter except when sulphuretted hydrogen is burnt. When hydrogen is burnt in pure liquid oxygen ozone is formed, but not hydrogen peroxide. When glowing wires and Nernst pencils were used, only ozone was detected, and in the arc, and with combustion processes in liquid air nitrous anhydride was also formed. The formation of ozone is not connected with the intermediate formation of higher oxides of nitrogen, and it is undoubtedly of a thermic nature when the Nernst pencil is used, and not a photo-chemical. Possibly in the arc light some of the ozone may owe its existence to ultra-violet radiation, while in the combustion of hydrogen it is a purely thermic action. The formation in the spark is undoubtedly affected by photo-chemical action. In liquid oxygen with the Nernst pencil a solution containing nearly 1 per cent of ozone can be prepared. The following table shows the results of the experiments:—

Source of heat.	In liquid oxygen.	In liquid air.	In atmos. air.
Glowing point	Ozone	Ozone	Nitric oxide
Nernst pencil	"	"	"
Arc	"	Ozone + nitric oxide	"
H-flame	"	"	"

MISCELLANEOUS.

Iron and Steel Institute.—President, Mr. Robert A. Hadfield.—The Annual Meeting of the Institute will be held at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 10th and 11th, 1906, commencing each day at 10.30 o'clock a.m. The Annual Dinner of the Institute is postponed until July 27th, 1906.

Programme of Proceedings.

Thursday, May 10th—

General Meeting of Members.

The Council will present their Report for the year 1905. The Hon. Treasurer will present the Statement of Accounts for 1905.

Scrutineers will be appointed for the examination of the Voting Papers.

Election of Officers and Council.

The Bessemer Gold Medal for 1906 will be presented to Mr. Floris Osmond (Paris).

The awards of the Andrew Carnegie Gold Medal and Research Scholarships for 1906 will be announced.

Friday, May 11th—

General Meeting of the Members of the Institution of Civil Engineers.

The following is a list of Papers that are expected to be submitted:—

"The Influence of Silicon, Phosphorus, Manganese, and Aluminium on Chill in Cast-iron." By E. Adamson (West Hartlepool).

"The Influence of Manganese on Iron." By Professor J. O. Arnold (Sheffield).

"The Relation between Type of Fracture and Micro-structure of Steel Tests Pieces." By C. O. Bannister, Assoc.R.S.M. (London).

"Compression of Steel Ingots in the Mould." By A. J. Capron, M.Inst.Mech.E. (Sheffield).

"The Manufacture of Rolled Solid Steel Car Wheels and Tyres." By P. Eyermann (Wisconsin).

"Brittleness in Thin Steel Sheets." By E. F. Law, Assoc.R.S.M. (London).

"Chainmaking Machinery." By E. Lelong (Couillet, Belgium).

"The Use of Oxygen in removing Blast-furnace Obstructions." By C. de Schwarz (Liège).

"Volume and Temperature Changes occurring during the Cooling of Cast-iron." By Professor Thomas Turner, M.Sc., Assoc.R.S.M. (Birmingham).

"The Influence of Copper in Steel." By F. H. Wigham (Wakefield).

The following reports on work carried out during the past year by holders of Carnegie Research Scholarships will be submitted:—

"Hardness of the Constituents of Iron and Steel." By Henry C. Boynton, D.Sc. (Cambridge, U.S.A.).

"Heat Treatment of Wire." By J. Dixon Brunton (Musselburgh).

"Quaternary Steels." By L. Guillet, D.Sc. (Paris).

"Influence of Carbon on Cast-iron." By W. H. Hatfield (Sheffield).

"The Preparation of Carbon-free Ferromanganese." By E. G. Ll. Roberts, and E. A. Wraight, Assoc.R.S.M. (London).

"Deformation and Fracture in Iron and Steel." By Walter Rosenhain, B.A., B.C.E. (Birmingham).

South African Association for the Advancement of Science.—The Meeting of the Association for the year 1906 will be held at Kimberley during the week ending July 14th, 1906, under the presidency of Mr. Gardner F. Williams. Special railway facilities will be afforded from all parts of South Africa, and arrangements are in progress for the carrying out of an instructive and interesting session. Members are earnestly desired to prepare papers for reading and discussion at the coming meeting as soon as possible, on any of the subjects in the four Sections, as follows:—(A) Astronomy, Chemistry, Mathematics, Meteorology, Physics. (B) Anthropology and Ethnology, Bacteriology, Botany, Geography, Geology and Mineralogy, Zoology, (C) Agriculture, Architecture, Engineering, Forestry, Geodesy and Surveying, Sanitary Science. (D) Archaeology, Education, Mental Science, Philology, Political Economy, Sociology, and Statistics. *Competitive Essay.*—The Council have accepted with many thanks an offer from Mr. E. B. Sargent to contribute the sum of £25 for the best essay on "The Best Means of Preserving the Traditions and Customs of the Various South African Native Races in a Form available for Future Scientific Research." Papers must be received by the Assistant General Secretary, Box 1183, Johannesburg, by December 1st, 1906. Each contribution must be signed with a *nom de plume*, and the *nom de plume* accompanied by the name and address of the author (who must be a Member of the Association) must be sent in a separate sealed envelope (marked "Essay" on cover) to the same address. The Papers will be adjudicated upon by an authoritative Committee whose decision will be published as soon afterwards as possible.—E. HOPE JONES (Cape Colony and Rhodesia), FRED. ROWLAND, F.C.I.S. (Transvaal, O.R.C., and Natal), Assistant General Secretaries.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Society of Arts, 8. (Cantor Lectures). "Ivory," by Alfred Maskell.

TUESDAY, 24th.—Royal Institution, 5. "Greek Classical Dress in Life and in Art," by Prof. G. Baldwin Brown, M.A.

WEDNESDAY, 25th.—Society of Arts, 8. "The Production and Collection of Picture Postcards," by Frederic T. Corkett.

THURSDAY, 26th.—Royal Institution, 5. "The Digestive Tract in Birds and Mammals," by Dr. P. Chalmers Mitchell, M.A.

— Society of Arts, 4.30. "Seistan," by Col. Arthur H. McMahon.

FRIDAY, 27th.—Royal Institution, 9. "Ore Deposits and their Distribution in Depth," by Prof. John W. Gregory.

— Physical, 5. "Some Simple Questions on the Images of Microscopes and Telescopes," by W. B. Croft. "A Gas Calorimeter," by C. V. Boys. "Lateral Vibration of Bars subjected to Forces in the Direction of their Axes," by J. Morrow.

SATURDAY, 28th.—Royal Institution, 3. "English Furniture in the Eighteenth Century," by Prof. Charles Waldstein, Ph.D., &c.

THE CHEMICAL NEWS.

VOL. XCIII., No. 2422.

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

PART II.—ANALYSIS OF THE TUNGSTEN GROUP.

By ARTHUR A. NOYES.

(Continued from p. 181).

Procedure and Notes.

Procedure 31.—Dilute the HF solution (P. 6) of the residue insoluble in HNO_3 with half its volume of water, cover the dish, and pass H_2S gas into the cold solution through a platinum or lead tube. [If the solution becomes dark coloured without yielding a precipitate, add at once 1 c.c. H_2SO_4 (1.84)]. Continue to pass the gas till the solution is completely saturated. Filter through a filter supported on a platinum-ring, collecting the filtrate in a platinum dish. Heat the filtrate nearly to boiling, pass H_2S into it for five minutes, and, if a precipitate forms slowly, continue to pass the gas for at least twenty minutes, and filter again. Wash the precipitate. (Precipitate, P. 32; filtrate, P. 33).

Notes.

1. No precipitation, either cold or hot, proves the absence of antimony, arsenic, and molybdenum. An orange precipitate in the cold shows antimony; a yellow one separating from the hot solution, arsenic; a brownish black one separating from the hot solution, molybdenum.

2. From the HF solution a large part of the antimony and of the arsenic, by far the larger proportion of the molybdenum, and all of the bismuth, copper, selenium, and tellurium, are precipitated. Tin and tungsten are not precipitated even when 500 m.grms. are present, nor is a larger proportion of either of these elements carried down, even when a small quantity (2–4 m.grms.) is present together with a large quantity (300–500 m.grms.) of antimony or molybdenum. Small quantities of lead (less than 6 m.grms.) are not precipitated.

3. The HF should be cold at first, and so dilute as to contain not more than 6 per cent HF, in order to secure the separation of 1 m.grm. of antimony, which then occurs even in the presence of 500 m.grms. of tin. Though this small quantity of this element is precipitated, a large quantity does not separate completely. The H_2SO_4 is added, when the colouration shows it to be necessary, to coagulate MoS_3 , which may otherwise remain in the colloidal state, and separate upon the subsequent addition of this acid as a gelatinous mass, which is difficult to filter, and which carries down with it other elements; the addition of the acid, if not necessary for this reason, is undesirable, since it prevents the separation of a quantity of antimony less than 2 m.grms. The solution is finally heated, and again treated with H_2S in order to cause the partial separation of even 1 m.grm. of arsenic. The passing of the gas is continued so as to precipitate a large proportion of the arsenic, antimony, and molybdenum, when these are present in considerable quantity.

Procedure 32.—Heat the H_2S precipitate (P. 31) with 5–10 c.c.† HNO_3 (1.20) until the sulphides are decom-

posed, adding some stronger HNO_3 (1.42) if necessary. Evaporate the solution to dryness, add HNO_3 (1.05), heat, and filter. (Filtrate, P. 51, uniting it with the main solution from P. 5; residue, reject).

Note.

1. The residue is treated with HNO_3 and the solution evaporated, so as to leave behind most of the antimony and molybdenum, the presence of which in large quantity in the main solution would somewhat increase the difficulties involved in the subsequent analysis of the H_2S precipitate. The filtrate is not likely to contain any element not also present in the main HNO_3 solution (P. 5), but it is well to unite the two solutions as a precaution.

Procedure 33.—[If it is not known from previous indications whether any element of this group is present, boil the filtrate from the H_2S precipitate (P. 31) till the H_2S is expelled, add 1 c.c. HNO_3 (1.42), evaporate nearly to dryness, pour into a platinum crucible, and evaporate to complete dryness; if there is a residue, dissolve it in a little HF].

To the filtrate from the H_2S precipitate (P. 31) [or to the HF solution of the residue after its evaporation as just described] add 2–3 c.c. H_2SO_4 (1.84), and evaporate till the acid fumes strongly. [If the liquid is dark coloured, add HNO_3 (1.42), and evaporate again]. Cool the solution, and pour it into 5 c.c. water. (Part of solution, P. 34; remainder, P. 35).

Notes.

1. A heavy yellow or greenish yellow residue proves the presence of tungsten; a blue colouration on the sides of the dish, that of molybdenum. The absence of these indications is inconclusive.

2. If SiO_2 was added to decompose fluorides (P. 3), the original residue insoluble in dilute HNO_3 (P. 5) may have consisted wholly of this substance, in which case it would be useless to continue the analysis of this group; hence the evaporation to dryness, in such a doubtful case, to see whether there is still a residue. Any SiO_2 present is volatilised as SiF_4 . HNO_3 is added to avoid volatilisation of TiF_4 , NbF_5 , and TaF_5 (P. 3, N. 4); and the solution, when nearly evaporated, is transferred to a crucible, so that a small residue may be more certainly detected. If it is doubtful whether the quantity of the residue is important; the crucible had best be weighed before re-dissolving the residue in HF, and afterwards weighed empty.

3. The evaporation with H_2SO_4 serves to expel all fluorine, which would prevent complete precipitation of the hydroxides of tantalum, niobium, and titanium at the next stage of the process, and attack the porcelain vessels used in the later operations.

4. Moderate quantities of all the elements that may be present are held in solution in the cold, diluted H_2SO_4 , except tungsten. This, if present alone in quantity as large as 2–4 m.grms., separates upon dilution as a white gelatinous precipitate, or if in large amount as a heavy yellow or greenish yellow powder, even before the H_2SO_4 is diluted. Niobium and tantalum, when present in large quantity, may also precipitate, especially if the liquid is allowed to become hot.

5. If much molybdenum is present, any portions of the substance on the sides of the dish above the concentrated H_2SO_4 solution may exhibit a deep blue colour, and the diluted solution may also be deep blue, owing to partial reduction to a lower oxide. In the presence of much molybdenum, the H_2SO_4 solution may also be brown or black owing to the formation of MoS_3 after the solution was filtered; in this case it is important to add HNO_3 to re-oxidise the molybdenum, since otherwise it will not dissolve completely on the following treatment with $(\text{NH}_4)_2\text{S}$.

Procedure 34.—Filter ½ c.c. of the H_2SO_4 solution (P. 33), if not clear already, add it to 5 c.c. $(\text{NH}_4)_2\text{MoO}_4$ solution,

* From the *Technology Quar ery*, xvii., No. 3.

† When, as in this case, a variable quantity of a reagent is given, it is to be understood that the quantity used is to be proportioned within the limits indicated to the amount of the precipitate or residue.

and heat the mixture to 60° or 70° . [If a precipitate results and if H_2S produced a precipitate in the HF solution (P. 31), dilute another $\frac{1}{2}$ c.c. portion of the H_2SO_4 solution with 3 c.c. water, place it in a test-tube in a steam-bath, pass H_2S into it slowly for twenty minutes, filter, boil the filtrate till the H_2S is expelled, and add it to 5 c.c. $(\text{NH}_4)_2\text{MoO}_4$ solution]. (Precipitate and solution, reject).

Notes.

1. No precipitation proves the absence of both phosphate and arsenate. The formation of a fine yellow precipitate proves the presence of one of these radicals, and after the treatment with H_2S , it proves the presence of phosphate.

2. Arsenic acid, especially on heating to boiling, gives a yellow precipitate entirely similar to that (consisting of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$) given by phosphoric acid. If therefore arsenic can be present, as shown by the formation of a precipitate with H_2S in the HF solution, it must be first removed as described in the bracketed part of this procedure.

3. To ensure sensitiveness in this phosphate test, it is necessary that the reagent be added in large excess, so as to diminish the solubility of the precipitate, and that the solution be warmed, so as to promote the formation of the complex phosphomolybdic acid. Under these conditions 0.1 m.grm. PO_4 is detected.

Procedure 35.—To the rest of the H_2SO_4 solution (P. 33) add cautiously NH_4OH (0.90) till the solution becomes alkaline; then add cautiously 5–10 c.c. colourless $(\text{NH}_4)_2\text{S}$, and digest in a covered casserole at 50 – 60° for fifteen to thirty minutes, with frequent stirring. Filter, using suction if the precipitate is large, and wash thoroughly with hot water. [If the precipitate is still orange coloured, return it to the casserole, heat it for ten to fifteen minutes with NH_4OH (0.96) diluted with an equal volume of water, and filter again]. (Precipitate, P. 36; filtrate, P. 39).

Notes.

1. No precipitation with NH_4OH proves the absence of tin, titanium, tantalum, and niobium; none with $(\text{NH}_4)_2\text{S}$ proves the absence of the last three of these elements. An orange-red filtrate proves the presence of molybdenum; a pure yellow one, its absence. A brown filtrate indicates the presence of vanadium.

2. NH_4OH precipitates the hydrates of SnO_2 , TiO_2 , Nb_2O_5 , Ta_2O_5 , and Fe_2O_3 completely. If present alone, H_2WO_4 passes completely into solution in NH_4OH , and both it and H_2MoO_4 remain in solution upon adding $(\text{NH}_4)_2\text{S}$. The SnO_4H_4 dissolves completely upon digesting with $(\text{NH}_4)_2\text{S}$; so do any quantities of tungsten, molybdenum, or vanadium that may be present with it. When the elements that give rise to an $(\text{NH}_4)_2\text{S}$ precipitate are present, tungsten and molybdenum may be carried down with them in considerable quantity, and the latter element imparts to the precipitate an orange or red colour, which is only very slowly removed by washing, but rapidly by digestion with NH_4OH . $(\text{NH}_4)_2\text{S}$ converts FeO_3H_3 to black FeS , the presence of which often gives rise to a dark coloured precipitate. Molybdenum, even in quantity of 1 m.grm., imparts an orange-red colour to the $(\text{NH}_4)_2\text{S}$ solution; vanadium gives a yellowish brown colour.

Procedure 36.—Transfer the precipitate insoluble in NH_4OH and $(\text{NH}_4)_2\text{S}$ (P. 35), with the filter if necessary, to a casserole. Pour over it a mixture of 5–15 c.c. 3 per cent H_2O_2 and 1–3 c.c. HCl (1.12); heat till the H_2O_2 begins to decompose rapidly, stir for two to three minutes, and filter through a washed filter, using suction if the residue is large. [If the residue is large and the solution strongly coloured, dissolve the residue in HF, and treat the solution of it again by P. 33, 35, and 36, omitting only the addition of $(\text{NH}_4)_2\text{S}$]. Wash the residue. (Residue, P. 37; solution, P. 38).

Notes.

1. A yellow or orange-red colouration of the H_2O_2 solution proves the presence of titanium; a colourless solution proves its absence. A residue undissolved by H_2O_2 is not a proof of the presence of tantalum.

2. When a large quantity of titanium is present, a considerable proportion of it may remain undissolved by the H_2O_2 and HCl , and this cannot usually be dissolved by treatment with a fresh portion of the mixture. Since the presence of much titanium interferes with the subsequent tantalum test, it must be removed by solution in HF, evaporation with H_2SO_4 , precipitation with NH_4OH , and re-treatment with H_2O_2 , as directed. Moderate quantities of niobium dissolve completely, or almost completely, in the mixture of H_2O_2 and HCl . Tantalum, whether present in small or large quantity, divides itself between the residue and solution, so that each contains, roughly, one-half of it. When tin and titanium are both present in the substance in considerable quantity, the former element is retained in large quantity in the $(\text{NH}_4)_2\text{S}$ precipitate, and a residue insoluble not only in H_2O_2 , but also in strong HF, is obtained. It may be brought into solution, if desired, by fusion with Na_2CO_3 and S.

3. The HCl is added to the H_2O_2 to promote the solution of the H_2TiO_3 , and to intensify the colour produced by it.

4. If titanium is present in quantity even as small as 0.1 m.grm., the H_2O_2 solution will have a distinct yellow colour. If present in quantity as large as 100 m.grms., the solution will have a deep orange-red colour. The production of this yellow or orange-red colour constitutes the test for titanium. When it is present alone in quantity as large as 2 m.grms., and niobium is absent in considerable proportion, a confirmation is furnished later by the reddish violet colour produced when zinc is added. To determine the approximate quantity present, the colour may be compared with that given by dissolving a weighed portion of pure TiO_2 in a little HF, evaporating with 1 c.c. H_2SO_4 (1.84) to the fuming-point, adding 10 c.c. H_2O_2 , and diluting measured portions of this solution till the same colour is obtained as that of the solution to be tested.

5. Vanadium in fairly small quantity also gives an orange-yellow or orange-red colour to H_2O_2 solution; but this element rarely remains with those of the tungsten group, and the small quantity that may be present with them passes into the $(\text{NH}_4)_2\text{S}$ solution. Molybdenum gives a pure yellow colour, but it is very much fainter at the same concentration. Tungsten gives no colour.

6. The yellow or red colour of the titanium solution is probably due to the formation of a double compound $\text{TiO}_2 \cdot x\text{H}_2\text{O}_2$.

Procedure 37.—Support the filter containing the precipitate insoluble in H_2O_2 and HCl (P. 36) upon a platinum ring, and pour through it repeatedly a portion of about 2 c.c. 48 per cent HF. Add to the solution 1 c.c. HNO_3 (1.42), and evaporate it just to dryness. Dissolve the residue in 1 c.c. HF, add 0.5 grm. solid K_2CO_3 , evaporate the solution to dryness, and heat the residue until, and only until, it becomes enamel white. Dissolve it in 2–3 c.c. of water, boil the solution down to about 0.5 c.c., add 0.5 c.c. water, and allow the solution to stand for ten minutes. If a coarsely crystalline substance separates, warm the liquid slightly, add water little by little until it is dissolved, and allow the solution again to stand for ten minutes. [If a coarsely crystalline substance separates in such large quantity that more than 2 c.c. water are required for its solution, add 1 c.c. H_2SO_4 (1.84), evaporate the mixture to the fuming-point, add it to 5 c.c. water, and treat the solution by P. 35, 36, and 37]. (Precipitate and solution, reject).

Notes.

1. A heavy white or greyish translucent viscous-

seeming precipitate, but not a coarsely crystalline or light flocculent one, proves the presence of tantalum; the non-formation of such a precipitate, its absence.

2. The HF solution is evaporated before adding the K_2CO_3 , to volatilise any SiO_2 that may have been taken up from the dishes and filter-paper used, for this may cause the tantalum to remain in solution. The HNO_3 is added to prevent any loss of tantalum by volatilisation (see P. 3, N. 4).

3. When much tantalum is present, a loose, white, crystalline precipitate of K_2TaF_7 forms when the K_2CO_3 is added; for 10 c.c. of the saturated solution of this salt in water to which a very small quantity of HF is added contains only 23 m.grms. Ta. But, when it is present in small quantity, it is necessary to remove the excess of HF by evaporation and ignition, and to boil the solution of the residue as directed, in order to convert this fluoride into the far less soluble oxyfluoride ($2K_2TaF_7 \cdot Ta_2O_5$). This oxyfluoride separates as a heavy, white, translucent, viscous-seeming powder of very characteristic appearance. If the residue is too strongly heated, the tantalum separates in a lighter, more flocculent, less characteristic form.

4. K_2TiF_6 is, like K_2TaF_7 , a difficultly soluble substance, 10 c.c. of its saturated solution in water at 20° containing 25 m.grms. Ti; and this may separate at the end of the tantalum test, in case the H_2O_2 failed to dissolve out all the titanium. It is readily distinguished, however, by its appearance in the form of white, semi-transparent, granular crystals, and it is re-dissolved by gentle warming and slight dilution of the solution, which have little effect on the tantalum compound after it has once separated.

5. K_2NbOF_5 is far more soluble than the double fluorides of titanium and tantalum; thus 10 c.c. of a saturated solution of K_2NbOF_5 at 20° contains 250 m.grms. Nb. When precipitated, it resembles K_2TiF_6 in appearance. The presence of a moderate quantity of niobium does not therefore, by its separation, interfere with the tantalum test; for even if a precipitate is produced in the very concentrated solution, it dissolves on the addition of a little water. Moreover, the presence of niobium does not prevent the separation of the $2K_2TaF_7 \cdot Ta_2O_5$.

Procedure 38.—Add 1—2 c.c. H_2SO_4 (1·84) to the H_2O_2 solution (P. 36) of the $(NH_4)_2S$ precipitate, and evaporate until the H_2SO_4 begins to fume strongly. Cool completely, pour the solution into 1 c.c. HCl (1·12), add a little granulated Zn, and let the action continue for two or three minutes, noting any colour effect. Dilute the solution with 4 c.c. water, and divide it into two parts. Pour one-third of it through a column of finely granulated Zn 5 c.m. in height, contained in a small straight drying tube (1—1·5 c.m. in diameter) whose bulb is stuffed tightly with glass-wool, and through which previously 5—10 c.c. HCl (1·02) have been poured, to make sure that the runnings are perfectly clear. Wash out the tube with 3—5 c.c. HCl (1·02). Allow the solution and washings to run directly into 5 c.c. of nearly saturated $HgCl_2$ solution to which 0·5 c.c. HCl (1·12) has been added. Note whether a precipitate forms immediately.

If no precipitate results, pour also the remaining two-thirds of the H_2SO_4 solution through the zinc column to confirm this fact. (Solution, reject).

If a precipitate results, proceed with the remaining two-thirds of the H_2SO_4 solution as follows:—Make alkaline with NH_4OH , add a sufficient excess to dissolve the precipitated $ZnO \cdot H_2O$, and filter. (Filtrate, reject). Transfer the precipitate, with the filter if necessary, to a platinum crucible, heat until the mass becomes dry and the filter is incinerated, mix the residue in a mortar with six times its volume of a mixture of equal weights of Na_2CO_3 and S, and heat the mixture in a covered porcelain crucible to a dull red heat for fifteen minutes. Cool, and treat the fused mass in the crucible with successive portions of hot water till it is disintegrated. Filter through a washed

filter and wash the residue. (Filtrate, P. 39, uniting it with the filtrate of P. 35). Transfer the precipitate, with the filter if necessary, to a platinum dish, and treat it with 5 c.c. 48 per cent HF till it is dissolved, continuing the treatment for some hours if necessary. Add 1—2 c.c. H_2SO_4 (1·84), and evaporate until the H_2SO_4 begins to fume strongly. [If the liquid is dark coloured, add HNO_3 (1·42), and evaporate again]. Cool, dilute with 5 c.c. HCl (1·02), and pour the mixture through a zinc column prepared as before, collecting the effluent in $HgCl_2$ solution. (Precipitate and solution, reject).

Notes.

1. A reddish violet colour appearing at once on the addition of Zn confirms the presence of titanium; a blue colour indicates that of niobium or tungsten. If there is no immediate precipitate in the $HgCl_2$ solution, this proves the absence of niobium; an immediate precipitate obtained in the first test shows the presence of niobium, tungsten, or molybdenum; if again obtained after the fusion with Na_2CO_3 and S, and if more than a mere turbidity, it proves the presence of niobium.

2. The solution is evaporated with H_2SO_4 to remove the H_2O_2 . It is then diluted with only a little HCl, and treated with a little Zn, so as to make the colour indications for titanium and niobium as delicate as possible.

3. If titanium is present alone in quantity as large as 2 m.grms., a distinct reddish violet colour is produced; if in quantity as large as 20 m.grms., a dark reddish violet colour results. If, however, a titanium solution containing HF—even the small quantity of it that remains after the evaporation of such a solution to slight fuming with H_2SO_4 —is treated with Zn, a green colouration is produced. If niobium is present alone in quantity as large as 0·5 m.grm., a pale blue colour results; if in quantity as large as 20 m.grms., a very dark blue colour is produced. When the reduction becomes complete, as is the case after the solution has been poured through the zinc column, a dark brown colour is obtained, even with a fairly small quantity of niobium. If titanium is present in predominating quantity, the niobium indication is obscured. Neither tantalum nor zirconium produces any colouration.

4. The salts both of titanium dioxide and niobium pentoxide are reduced to a lower state of oxidation (Ti_2O_3 and Nb_2O_3 , respectively) by the nascent hydrogen; but the lower oxide of niobium alone has sufficient reducing power to convert $HgCl_2$ into $HgCl$. The test is delicate, but not very characteristic. Neither tantalum, zirconium, titanium, iron, nor tin produces the same result under the conditions of the experiment; but titanium in large quantity may do so if the $HgCl_2$ solution is allowed to stand, even for fifteen minutes. Tantalum or zirconium is not reduced at all by Zn, and tin is reduced to the metallic state. Iron is converted into a ferrous salt, but this does not reduce $HgCl_2$. The lower oxides of tungsten, molybdenum, and vanadium (WO_2 , Mo_2O_3 , and V_2O_2) produced by the action of Zn do, however, cause reduction of $HgCl_2$; moreover, these elements are retained in considerable quantity in the $(NH_4)_2S$ precipitate, when much titanium is present. If a precipitate forms in the $HgCl_2$ solution, it may therefore arise from one of these elements and not from niobium; and it is then necessary to remove them from the remaining two-thirds of the H_2SO_4 solution by fusion with Na_2CO_3 and S, and again apply the reduction test. Repeated digestion of the $(NH_4)_2S$ precipitate with NH_4OH and $(NH_4)_2S$ is much less effective. Even after the fusion with Na_2CO_3 and S, traces of tungsten may remain in the titanium residue if much tungsten was present in the solution treated with $(NH_4)_2S$; and a slight turbidity (not more than that given by 1 m.grm. Nb) may result therefrom in the second test with Zn and $HgCl_2$. In such a case, a very slight turbidity must not therefore be regarded as proof of the presence of niobium, but a considerable one is conclusive evidence of it. A

quantity of niobium as small as 2 m.grms. may be lost in the processes connected with the fusion, but not a larger quantity.

5. The fusion with Na_2CO_3 and S is also necessary, in order to make possible the detection of small quantities of tungsten, which are carried down almost completely with the titanium hydroxide when much of this is present. It is on this account also that the aqueous solution of the fused mass is united with the original $(\text{NH}_4)_2\text{S}$ filtrate.

(To be continued).

A REVISION OF THE ATOMIC WEIGHTS OF SODIUM AND CHLORINE.*

By THEODORE WILLIAM RICHARDS
and
ROGER CLARK WELLS.

(Continued from p. 183).

PREPARATION OF PURE MATERIALS (continued).

Silver,

RE-CRYSTALLISED silver nitrate served as the starting point for the first specimens, and the already purified residues from the early experiments were again converted into pure silver for later use. Many samples were prepared from different sources.

The silver used in all the experiments on sodic chloride was at first purified by precipitation as chloride and then recovered by reduction of the chloride with invert sugar and sodic hydroxide. While it is true that this process is not the best for the final treatment of the silver, the precipitation as chloride is an excellent step in the preliminary purification. The invert sugar was made from a filtered solution of "rock sugar." No metals were found in it by electrolytic treatment. The sodic hydroxide used, after settling and decantation, had been electrolysed until iron was completely removed. This slow but effective way of removing foreign metals was hastened by using a rotating cathode, while a fixed anode stirred the solution. The argentic chloride was precipitated from a somewhat dilute solution, to avoid the occlusion of impurities, and must be thoroughly washed. It is best to wash at first with cold water, in order to avoid the contraction of the precipitate. The reduction was carried out in a silver dish to avoid the introduction of silicates. This precaution is not needed when electrolytic purification is to follow. In some cases, where the original material was not wholly free from suspicion, the precipitation as chloride and reduction were repeated. After reduction, the washed silver was fused upon either sugar charcoal or pure lime, before the blast-lamp, whose nozzle was scrupulously cleaned. If the large buttons of metal thus formed are not kept hot too long and are cooled in a reducing flame, they are already extremely pure. (Richards, *Proc. Am. Acad.*, 1893, xxix., 65; *Zeit. Anorg. Chem.*, 1893, vi., 98; see also *Proc. Am. Acad.*, 1903, xxxviii., 450. This work was confirmed in the latter part of the present investigation.) For ordinary work, or even for work on atomic weights of usual accuracy, its purity suffices. Nevertheless, it cannot be considered as perfectly pure, for it must contain, perhaps, 0.001 per cent of sulphur and variable traces of carbon from the illuminating gas (or else oxygen from the air), as well as an occasional trace of argentic chloride, arising from incomplete reduction. When thus cooled it is likely to contain numerous minute cells inclosing gas.

As one stage in the purification the electrolytic method used by J. L. Hoskyns Abrahall has many advantages (*Journ. Chem. Soc. Trans.*, 1892, lxi., 660). The almost pure material just described is made the anode of a cell

containing a concentrated solution of argentic nitrate prepared from the same silver. The cathode is a pure silver wire, upon which is deposited by a properly regulated current beautiful crystals of electrolytic silver. The finely crystalline powder which falls from the anode (Richards and Heimrod, *Proc. Am. Acad.*, 1902, xxxvii., 415) may be easily collected separately by placing the anode button in a watch-glass or low dish, wholly submerged in the electrolyte. In order to exclude every chance of contamination, no metal but silver may be allowed to come in contact with the electrolyte, although the danger from an immersed platinum wire, either at cathode or anode, is obviously slight. Three samples of silver were thus prepared, called respectively M, N, and P. This silver must have been free from every conceivable impurity, except about 0.02 to 0.05 per cent of the mother-liquor from which it was deposited (Richards and Heimrod, *Proc. Am. Acad.*, 1902, xxxvii., 415; Richards, *Proc. Am. Philos. Soc.*, 1903, xlii., 28; *Zeitsch. Phys. Chem.*, 1903, xlv., 189). This important impurity, consisting wholly of water and argentic nitrate, can be eliminated only by fusing the silver, a matter which will soon be discussed.

Besides this very pure material used in the work on sodium, several new samples of at least equal purity were made for the even more critical work on chlorine. Three of these new preparations were made from thrice crystallised pure argentic nitrate. A portion of this nitrate was converted into argentic chloride and reduced by pure invert sugar and purified sodic hydroxide. A second portion was reduced by the invert sugar and sodic hydroxide. A third portion was reduced by ammoniac formate and ammoniac acetate as recommended by Stas ("Oeuvres," iii., 40). Some of each of these lots was deposited by electrolysis in a concentrated silver nitrate bath in the usual way (S, T, U, respectively).

Not content with these preparations—although all appeared to be equally pure—and anxious to leave no stone unturned whose lifting might disclose some new source of error, we made yet two more preparations with new precautions. For one of these, through the great kindness of Mr. Richard Pearce, of the Boston and Colorado Smelting Works at Argo, Colorado, a specimen of metal was secured whose source and history were known as far back as possible. Below is given Mr. Pearce's statement concerning it:—

"This specimen is the product of the treatment of ores mainly from Colorado, in which it occurs associated with quartz, barite, calcite, pyrite, sphalerite, with more or less copper in the form of chalcopryite, together with small quantities of arsenic, antimony, lead, bismuth, and tellurium. The silver minerals are chiefly argentite, polybasite, pyrrargyrite, proustite, tetrahedrite, stephanite, and occasionally cerargyrite. A small percentage of the silver comes in copper mattes purchased in other districts, more particularly Montana, where the silver ores are much the same in character, and are smelted with copper ores, forming a matte containing about 200 ounces of silver per ton.

"The roasted ore is mixed with others, principally siliceous, and the mixture is so arranged that, when smelted, it shall yield a slag containing as near as possible 40 per cent of silica and a first matte or fusible sulphide which assays 40 per cent of copper, 400 ounces of silver, and 6 ounces of gold per ton.

"The first matte always contains a certain amount of lead, but the quantity rarely exceeds 10 per cent. The next stage in the process includes the roasting and concentration of the ore-metal, or first matte, to "white metal" containing 60 per cent. of copper.

"This white metal is now ready for the extraction of the silver, which comprises the following operations:—Rough roasting; fine grinding; fine roasting for sulphate of silver by Ziervogel's process; leaching, and the precipitation of the silver on plates of copper.

"In the precipitation of the silver a certain amount of copper is found mixed with the silver in the form of

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† According to Stas, saccharose at 100° would have answered as well as invert sugar at 60°. The saccharose is, of course, inverted by the strong hot alkali ("Oeuvres," iii., 13).

cuprous oxide and of small scales and scraps of metallic copper, and a process of refining is necessary previous to melting. This copper is removed by prolonged boiling with water containing a small quantity of sulphuric acid, into which air is injected by means of a small jet of steam. Sulphate of copper is formed, which is carefully washed out of the silver. The silver is then dried and melted into bars of an average fineness of 99.9 per cent."

The silver came to us in the granulated form obtained by dropping into water, and having been prepared with unusual care, was found to be even purer than Mr. Pearce claimed. After solution in nitric acid, it was crystallised fifteen times from acid solutions with centrifugal draining. The solubility in cold nitric acid is so slight that this train of purification could be effected without serious loss. Even after the second crystallisation the salt was free from any observable trace of copper, and all other metallic impurities must have been eliminated before the last crystals were obtained. The pure argentic nitrate was dissolved in pure water and precipitated by hot ammoniac formiate, prepared from pure freshly distilled formic acid and ammonia which had been collected in platinum. It is better to use pure ammoniac formiate instead of a mixture of ammoniac formiate and acetate as Stas did, because in the former case less carbon is included in the cells of the crystals, and moreover, that which it included occurs in a less dangerous form. Since the reaction takes place according to the equation $2\text{AgNO}_3 + 2\text{HCOONH}_4 = \text{Ag}_2 + 2\text{NH}_4\text{NO}_3 + \text{CO}_2 + \text{HCOOH}$, every 170 grms. of argentic nitrate need 46 grms. of pure formic acid (or about 42 c.c. of 90 per cent acid, with specific gravity 1.2) converted into ammoniac formiate. It is necessary to take this double amount in order that the ionised hydrogen (nitric acid) may be removed by the salt of the weaker acid. The precipitation was conducted in good glass. The beautiful white precipitate was washed with the purest water, until the washings gave no Nessler test. This silver, V, although it had not been electrolysed, was as pure as any which we made, judging from the analysis. (The preparation work and analyses of this silver were conducted wholly by T. W. Richards). The method of purification just described is the most convenient and safest of all. The only improvement which might be suggested is the use of a silver dish for conducting the final precipitation. This improvement was tried in the next preparation.

Part of the silver, not electrolysed, proceeding from the earlier reduction with ammoniac formiate and ammoniac acetate (see above) was dissolved in re-distilled nitric acid. The silver nitrate, once more crystallised, was dissolved in pure water in a large silver dish. Ammoniac formiate was freshly prepared by passing pure ammonia gas into re-distilled formic acid. With it the silver nitrate was reduced in a silver dish, but otherwise, as described above, washed free from ammonia and dried in the same silver dish. This sample was called W.

There is no reason to believe that any of these samples of silver contained any appreciable impurity, except the traces of included mother-liquor already alluded to. It is probable that Stas's silver also was equally pure at this stage in the proceedings. The subsequent treatment of the silver, in the effort to eliminate the mother-liquor and prepare the metal for weighing, seemed to be in our experiments the only cause of difference in the quantitative behaviour of our samples, and there is every reason to believe that Stas introduced during this treatment the impurities which have rendered a revision of his work imperative.

Because of this importance of the subsequent treatment, it is necessary to record a very detailed statement of the precise operations of the present research in this particular, and to point out the differences between these operations and the methods of Stas.

Everyone must agree that fusion alone is the only safe method of eliminating wholly the liquid included in the cells of the crystals, whether these crystals be produced by electrolytic or chemical reduction. The difficulty is to find

an environment for the silver during its fusion from which it will not absorb or retain foreign substances.

The question presents a twofold difficulty, because both the solid support of the silver and the atmosphere which surrounds it must be considered. The former of these difficulties may be discussed first.

In what vessel may the silver be fused, in order to avoid contamination? Stas, in his posthumous work, recommends fusion in a cupel of basic calcic phosphate, in the flame of a blast-lamp, and subsequent ignition in hydrogen. This process, while possibly as good as he contends, may nevertheless be a dangerous one. Everyone knows the risks to a platinum crucible of igniting in it a phosphate with reducing material, and yet Stas took no steps to prove the absence of traces of argentic phosphide from the metal prepared in this way. His own observation, indeed, confirms this suspicion, for he states that silver thus fused in an oxidising flame became covered with a yellow crystalline film, which instantly disappeared in a reducing flame. The great instability of the oxide of silver affords reason for doubting his assumption that this film was an oxide; it seems more probable that it was a phosphate, produced by oxidation of silver phosphide, and decomposed by reduction to this compound again. Stas, relying entirely upon the superficial appearance of the silver and its flame test as a guide to its purity, would not have discovered the presence of phosphide.

The possibility of this danger is enough to incline the careful chemist to avoid the presence of phosphorus. As a matter of fact, Stas never used silver prepared in this way for his atomic weight researches (Stas, "Ouvres" Compl., iii., 75), and no one else seems to have used this procedure except A. Scott (*Journ. Chem. Soc. Trans.*, 1901, lxxix., 147), who fused 5 grms. of silver in this way for a single analysis. Of course, however, a single analysis is too slender a basis upon which to form any adequate judgment concerning its purity. Actuated by the preceding considerations, we did not take the trouble to test the method, preferring first to test others which gave more promise of satisfactory results.

Another possible material, which has been partially tested in previous work, is carbon. Sugar charcoal may be prepared in a state very free from metallic impurities, and would serve excellently if it were not that carbon is probably soluble to a slight extent in the molten metal. We gave this possibility a fair test, and found that when the silver is fused on a cupel of sugar-charcoal with a clean blast-lamp and moderately pure illuminating gas, it is, as a matter of fact, very pure. (Experiments 67, 68, and 71). Probably the oxidising flame used to melt the metal prevents the introduction of much carbon at first, and during the brief reducing period in which the metal must be cooled to eliminate an excess of oxygen there is not time to dissolve much carbon. Evidently, however, a process which depends upon the mutual elimination of opposing errors is an uncertain one, and hence not suitable for the most accurate work. That carbon is really dissolved was well shown by another experiment, in which a carbon boat in a porcelain tube filled with pure hydrogen was used to contain the fusing silver. The experiment yielded silver slightly less pure than the previous average; it must have contained 0.005 per cent of dissolved carbon. (Expt. 79). Of course, however, a single experiment has but little exact weight in such a case, except to show that the process is probably undesirable.

Returning from these unsatisfactory methods to the one used very early in his career by Stas, we tested once more the use of lime as a support for the fusing silver. This seemed to be an especially appropriate substance for the containing vessel, because it is so easily obtained pure, and because it is so hard to reduce that no metallic calcium could be dissolved by silver. But of course the silver must be saturated with dissolved lime, and it remained to be proved that a saturated solution of lime in fused silver is so dilute as to introduce only a wholly insignificant amount of impurity. This was easily shown by actual experiment.

Ten grms. of silver fused on lime were dissolved in pure dilute nitric acid in a platinum dish, and precipitated as sulphide by pure hydrogen sulphide gas, led in through a platinum tube. After filtration on a platinum funnel, the remaining liquid was evaporated to dryness in platinum. The minute trace of residue, probably due to traces of dust, on moistening with hydrochloric acid gave no trace of the calcium bands in a spectrometer which showed them plainly from a solution containing 0.01 m.grm. of lime in 1 c.c. Hence it is evident that less than this amount of lime was dissolved by the silver, *i.e.*, less than 0.0001 per cent, if any.

This experiment settled the question concerning the supporting substance, but of course the lime must be perfectly pure. If the lime is partially made from the nitrate, it must be very thoroughly ignited before it is used, otherwise the silver may dissolve some of the oxygen caused by the decomposition of the salt. This was shown by the careful testing of a quantity of silver fused on a new boat, which had not been thoroughly ignited. (Expts. 72 to 76). A boat in which pure silver has already been fused has an advantage in this respect, as well as because every accessible trace of reducible material must have been dissolved out of it. Of course the lime used in the present experiments was especially purified, as will be related.

It is true that even when carefully prepared a boat of lime is likely to be so friable as occasionally to cause a partial coating of the button of silver with the powdered lime, but the great surface tension of molten silver keeps this all on the surface, whence it is easily dissolved by means of the dilute nitric acid always used by us to clean the metal. Scott, who has objected to the use of lime, again on the basis of a single experiment, does not mention having taken this necessary precaution.

All the silver used in the three final series of experiments which follow was thus ignited in pure well-seasoned lime boats, capable of holding from 30 to 50 grms. at each fusion. The unglazed porcelain boats in which the lime was moulded were made on purpose for this object by the Royal Berlin Porcelain Manufactory.

The enviroing atmosphere around the silver during fusion next claims attention, since that, too, may vitiate molten metal. Obviously air is impossible. A vacuum seemed *à priori* to be the best means of preventing the access of impurity, but, to our surprise, we found that silver fused in a vacuum was sometimes less pure than that fused in the open flame of the blast-lamp. (Expts. 72 to 76). This puzzling circumstance was ascribed finally to the supersaturation of silver with oxygen, derived either from included argentic nitrate or from the calcic nitrate in the boat. (A trace of chlorine, which, however, could hardly have been present, would have the same effect). Silver precipitated by formiate ignited on a pure boat does not show this impurity, because free from oxidising substances; and a few minutes' ignition in pure hydrogen quickly removes in chemical fashion this supersaturation when it exists, thus purifying the silver. The amount of hydrogen which remains must be on the limit of the weighable; at least, we were unable to detect it quantitatively, because silver fused in hydrogen yielded exactly the same amount of argentic chloride as that containing no oxygen which had been fused in a vacuum. This is shown by the comparison of Expts. 77, 78, 80, 81, 83, and R. 2, with 84, 85, and R. 3. Hence Stas's conclusion that silver does not dissolve over 0.0004 per cent of hydrogen is supported, although indeed his method of preparing the silver was somewhat different from ours, and his method of distinguishing the hydrogen was somewhat doubtful.

The discovery of the residual trace of oxygen in the fused electrolytic metal, which had contained occluded nitrate, was not made until the work on sodium was finished, but fortunately three pieces of the silver used in that work still remained, so that it could be compared with the purest silver which we were able to make. The comparison was made by weighing the chloride obtainable from known weights of each sample, and the details will

be recorded in full in the chapter concerning the synthesis of this salt. For the present it is enough to say that the silver used in the work on sodium yielded 0.004 per cent less chloride than the purest silver, and therefore was assumed to contain that percentage of impurity. (The average of analyses, 65, 66, 70 was compared with the average of the final series. See *prox.*). A change of only 0.002 in the atomic weight of sodium was caused by this difference.

All the silver used in the final series of syntheses of silver chloride was free from dissolved oxygen, and three of the specimens must have been free from hydrogen also. The method of treating each is sufficiently specified in the table of results, and need not be further discussed here. The silver used in this part of the work was the purest we were able to prepare, and we know of no impurities which it could have contained, except in some cases the insignificant trace of hydrogen already mentioned.

The boat used for the fusion was made from a mixture of pure lime and calcic nitrate, and was contained in a porcelain tube closed with Hempel stoppers. The tube was heated to bright redness in a Fletcher furnace (*Proc. Am. Acad.*, 1895, xxx., 379). The resulting bars of silver were freed from the adhering lime by scrubbing with clean hard sand and successive treatments with dilute nitric acid. The argentic nitrate was dissolved away by ammonia, and many washings with water were followed by drying the bar in a hard glass tube at about 400° in a vacuum. (The silver used in Experiments R 1, R 2, and R 3 was wrapped in pure silver foil during this ignition to prevent contact with hot glass). Water might otherwise become sealed into the microscopic cavities, often present in fused silver, during the next operation of cutting into blocks. The cutting is best carried out upon a silver plaque by means of a clean steel cold chisel. The blocks thus cut were superficially etched once more with nitric acid, so dilute that a possible trace of iron could not assume the passive state, and the cleaning and drying operations were repeated. The pieces when preserved in a desiccator over potash are ready for weighing and analysis.

After the details of the analysis have been discussed, the relation of the purity of this silver to that of Stas will be made clear.

Lime.

The preparation of pure lime upon which to fuse the silver was a matter of great importance, because of the danger that any impurity in it might contaminate the silver. Its preparation was begun by dissolving marble in nitric acid, boiling with an excess of calcic hydroxide, filtering, neutralising, and twice re-crystallising the calcic nitrate. (Calcic nitrate should be re-crystallised below its transition temperature, 44°, a proceeding much facilitated by inoculation with the respective hydrate). Calcic carbonate was then precipitated with ammoniac carbonate, repeatedly washed, and finally dissolved in re-distilled nitric acid.

The resulting nitrate, made alkaline with ammonia, was electrolysed to remove a suspected trace of iron, and filtered through a layer of calcic carbonate upon a Gooch crucible. It was found that ammoniac carbonate, of variable composition, could be conveniently distilled with steam from its solution. With such a distillate, prepared wholly in platinum, calcic carbonate was again precipitated and well washed. A small portion of this was converted into nitrate.

Ignition of the calcic carbonate to oxide was carried out in porcelain, since platinum is slightly volatile at high temperatures, and might have contaminated the lime. A dry mixture of calcic oxide, with about a fifth its weight of powdered anhydrous nitrate, was packed into specially made large unglazed boats of Berlin porcelain. The moulded mixture when heated to redness sintered firmly together and made a chemically pure receptacle, large enough to contain about 50 grms. of silver at a time. In order to prevent adhesion of the boat to the glaze of the porcelain tube, the boat should not fit the tube very closely,

and it is well to cover the glaze under the boat with a layer of pure powdered lime.

Utensils.

Of course all the containing pieces of apparatus—dishes, funnels, crucibles, retorts, condensers, and so forth—were of platinum wherever silica was to be feared and platinum was not itself harmful. In this latter case, according to circumstances, either silver vessels or vessels of the best insoluble glass (Jena or "nonsol") or porcelain, or in some cases fused quartz, were used. In this way the greatest possible purity of the preparations was assured.

(To be continued).

THIRTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1905.*

By F. W. CLARKE.

(Continued from p. 184).

Strontium.

In 1894 Richards published his determinations of the atomic weight of strontium, which were based upon analyses of the bromide. A little later he made another set of measurements upon the chloride, which did not accord sufficiently well with the bromide series. The discrepancy is now explained by the discovery that the then accepted value for chlorine was too low, and the actual work upon strontium chloride has proved to be satisfactory. The data now published by Richards (*Proc. Amer. Acad.*, xl., 603; *Zeit. Anorg. Chem.*, xlvii., 145) are given below; they represent vacuum weights, and refer to Ag = 107.93 and Cl = 35.473.

Weight SrCl ₂ .	Weight Ag.	Ratio, 100 Ag ₂ to SrCl ₂ .
4.2516	5.7864	73.476
2.4019	3.2688	73.480
3.5184	4.7886	73.475
3.0264	4.1189	73.476
Mean		73.477

Hence Sr = 87.661 as compared with 87.663 from the bromide.

Copper.

Incidentally to his work on the atomic weight of tellurium, Gallo made a few electrolytic precipitations of copper in comparison with silver (*Gazz. Chim. Ital.*, xxxv., 261; atomic weight computed with Ag = 107.93). The corrected data are as follows:—

Weight Cu.	Weight Ag.	Atomic weight Cu.
0.21805	0.73937	63.66
0.27153	0.92062	63.65
0.19001	0.64571	63.52
0.39585	1.34578	63.50
Mean		63.58

Cadmium.

Baxter and Hines, in re-determining the atomic weight of cadmium, have made use of the chloride (*Journ. Am. Chem. Soc.*, xxvii., 222). Both of the usual ratios were measured, and the corrected data, reduced to vacuum weights, are given below.

Ratio CdCl₂ : 2AgCl.

Weight CdCl ₂ .	Weight AgCl.	Atomic weight Cd.
5.53241	8.65336	112.475
7.77758	12.16166	112.471
8.87917	13.88344	112.481
Mean		112.476

Weight CdCl ₂ .	Ratio CdCl ₂ : 2Ag. Weight Ag.	Atomic weight Cd.
4.92861	5.80063	112.463
3.86487	4.54891	112.454
5.08551	5.98569	112.451
5.84335	6.87704	112.468
5.99952	7.06084	112.468
3.73092	4.39095	112.467
Mean		112.462

The calculations were made with Ag = 107.93 and Cl = 35.473. Additional data are promised relative to cadmium bromide. The mean of the two series, as given by Baxter and Hines, is Cd = 112.469.

Aluminium.

The work of Kohn-Abreast on the atomic weight of aluminium was noticed in the report for 1904; it has since been published in detail (*Bull. Soc. Chim.*, [3], xxxiii., 121). Impure aluminium, but containing known impurities, was dissolved in hydrochloric acid, and the hydrogen evolved was burnt over copper oxide and weighed as water. The following uncorrected amounts of water were furnished by 100 parts of the metal.

98.08
98.20
97.86
98.10
98.44
98.03
97.98

The mean, corrected for the impurities in the aluminium, is 99.151. Hence Al = 27.05 when H = 1; with O = 16, Al = 27.25.

Two additional experiments were made upon the conversion of aluminium into oxide, as follows:—

0.3429 Al gave 0.6444 Al ₂ O ₃ ; Al = 27.09.
0.4168 Al gave 0.7850 Al ₂ O ₃ ; Al = 27.03.

The degree of concordance shown by these determinations is not satisfactory; neither were the methods by any means unimpeachable.

Silicon.

The determination of the atomic weight of silicon by W. Becker and J. Meyer (*Zeit. Anorg. Chem.*, xliii., 251) was effected through the conversion of silicon tetrachloride into the dioxide. The chloride was decomposed by ice-water under suitable precautions, which are fully described. After decomposition, the mixture was evaporated to dryness and the silica was ignited and weighed. In a supplementary investigation by Meyer (*Zeit. Anorg. Chem.*, xlvii., 45) the possible retention of chlorine by the silica was carefully examined, and that impurity was proved to be absent. The final data, referred to vacuum weights, are given below, as published in the second of the two papers. The atomic weight was computed with Cl = 35.470.

Weight SiCl ₄ .	Weight SiO ₂ .	Atomic weight Si.
4.16733	1.47597	28.259
4.69585	1.66304	28.253
4.91918	1.74204	28.248
5.37434	1.90349	28.260
5.93985	2.10364	28.254
6.73605	2.38570	28.257
7.16361	2.53606	28.220
7.82779	2.77242	28.259
Sum .. 46.82400	16.58236	Mean 28.251

The value adopted by Meyer is Si = 28.25. This is lower than the 28.4 derived from Thorpe and Young's analyses of the bromide.

* From the *Journal of the American Chemical Society*, xxviii., No. 3.

Lead.

In an interesting paper upon the lead voltameter, Betts and Kern give two series of determinations of the electrochemical equivalent of lead (*Trans. Amer. Electrochemical Soc.*, vi., 67). The metal was deposited in direct electrolytic comparison with silver from an acid solution of lead fluosilicate. The weights deposited and the corresponding equivalents were as follows, the atomic weight of silver being taken as 107.93.

Weight Ag.	Weight Pb.	Equivalent Pb.
<i>First Series.</i>		
5.8958	5.6221	102.90
5.8958	5.6396	103.24
5.7863	5.5246	103.04
5.7863	5.5450	103.43
7.8408	7.5108	103.39
7.8408	7.5168	103.47
7.6253	7.3191	103.59
7.6253	7.3221	103.62
6.2287	5.9600	103.27
6.2287	5.9605	103.28
16.6804	15.9996	103.52
16.6804	16.0014	103.54
6.8652	6.5815	103.47
6.8652	6.5812	103.46
9.3253	8.9390	103.46
9.3253	8.9419	103.49
6.8566	6.5695	103.41
6.8754	6.5877	103.41
<i>Second Series.</i>		
9.0470	8.6678	103.41
9.0470	8.6663	103.39
13.4113	12.8607	103.49
13.4113	12.8558	103.46
7.2780	6.9716	103.39
7.2780	6.9755	103.44
7.2738	6.9695	103.41
7.2738	6.9698	103.42
6.5278	6.2550	103.42
6.4864	6.2168	103.44

The mean of the determinations in the first series gives an equivalent of 103.39, or Pb = 206.78; from the second series Pb = 207.86. As the object of the investigation was to ascertain the availability of the lead voltameter for exact work, and not to determine an atomic weight, these values cannot be utilised directly. They show, however, some promise, and indicate that the process used might be developed into a good method of determination. The suggestiveness of the data warrants their reproduction here.

(To be continued).

Industrial Preparation of Calcium Hydride.—Georges F. Jaubert.—Finely-divided metallic calcium, as M. Moissan has shown, when heated absorbs a molecule of hydrogen, giving a hydride corresponding to the formula CaH_2 . This hydride, under the action of water at ordinary temperatures, is decomposed in the same manner as calcium carbide, giving a brisk evolution of pure hydrogen, $\text{CaH}_2 + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + 2\text{H}_2$. The author devises an industrial preparation for this new product. The metallic calcium is prepared by electrolysis of melted calcium chloride. The electric energy necessary to prepare 100 kilograms of metallic calcium in twenty-four hours is about 20 volts and 7500 ampères. The hydride is manufactured from this by heating the metallic calcium in spiral vessels kept at a high temperature. Round these circulates a current of gaseous hydrogen, which the calcium gradually absorbs. After some hours of heating, all the calcium is transformed into the hydride.—*Comptes Rendus*, cxlii., No. 13.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 5th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

THE PRESIDENT announced the donation by Mr. John Spiller of a Berzelius medal in selenium which had been in the possession of the donor during the past fifty years.

It was also stated that the Council had appointed the following Committees:—

Finance Committee—E. G. Hooper, G. T. Moody, H. T. Brown, T. E. Thorpe, W. A. Tilden, and the Officers.

House Committee—W. R. Dunstan, J. E. Reynolds, W. J. Russell, J. M. Thomson, T. E. Thorpe, W. A. Tilden, and the Officers.

Library Committee—E. C. C. Baly, B. H. Brough, F. D. Chattaway, B. Dyer, A. Harden, C. A. Keane, A. Lapworth, E. J. Mills, J. Millar Thomson (Chairman), J. A. Voelcker, J. Wade, the Editor, and the Officers.

Publication Committee—H. E. Armstrong, E. C. C. Baly, B. Dyer, E. J. Mills, W. A. Tilden, J. Wade, and the Officers.

Research Fund Committee—H. T. Brown, W. R. Dunstan, P. F. Frankland, A. D. Hall, G. Matthey, R. Messel, H. Müller, W. H. Perkin, jun., S. P. U. Pickering, W. A. Tilden, and the Officers.

Messrs. T. V. Barker, and I. B. Hobsbaum were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Percy Corlett Austin, M.A., Queen's College, Galway; Lionel John Drinkwater, 27, Stokenchurch Street, Fulham, S.W.; Bernard Flurscheim, Ph.D., Heatherlands, Fleet, Hants; Edgar Percy Hedley, 6, Royal Terrace West, Kingstown, Co. Dublin; Arthur Edwin Hill, 236, Willesden Lane, Brondesbury, N.W.; Frederick Gowland Hopkins, M.A., M.B., D.Sc., F.R.S., Stafford House, Newnham, Cambridge; Thomas Macdonald, North Frodingham, Driffild, Yorkshire; Harold Lawson Pendlebury, 4, Wentworth Street, Bolton; Percy George Pennymore, Eskbank Iron and Steel Works, Lithgow, N.S.W.; Walter Hansen Rawles, 81, Lewisham High Road, S.E.; John Senior, Sizing Hill, Batley Carr, Dewsbury; Emanuel George Stirmer, Park House, Margery Park Road, Forest Gate, E.; Richard Lumley Treble, B.Sc., The School Lodge, Cranbrook, Kent; Robert Hutchison Turnbull, Messrs. MacAndrews and Forbes Co., Smyrna, Turkey-in-Asia; Charles Wightman, 43, Portland Place, W.

Of the following papers, those marked * were read:—

*67. "An Improved Apparatus for Measuring Magnetic Rotations and obtaining a Powerful Sodium Light." By WILLIAM HENRY PERKIN, sen.

The author dealt with the advantages and disadvantages of the ordinary electro-magnet with pierced pole-pieces, and also the long coil or helix as a means of obtaining a magnetic field suitable for the measurement of magnetic rotations, and the desirability of obtaining an apparatus which shall possess all the advantages without the disadvantages of either of these systems. This has been effected by using a short but very powerful coil and a powerful electric current. The coil is cased with steel and has a three-inch gun-metal tube through the centre, the interior of this being the position of the magnetic field. The glass measuring tubes are supported in this tube in a metal trough which can be kept at any required temperature. Reference was also made to the measurement of the plane of polarisation and the difficulties which arise from the fact that the sodium flame is not purely monochromatic. This defect was especially felt when measuring large rotations, and was successfully

overcome by the use of a direct vision prism attached to the eye-piece or placed in the telescope of the analyser; through this a distinct image of the half-shadow disc is observed; this disc is on the analyser in the apparatus used: the prismatic colours arising from the impurity of the sodium flame are seen on either side of the image. Lastly, a method of obtaining a powerful sodium light was described, which consists in employing a large Bunsen burner with a fine tube up the centre which is supplied with oxygen. This burner, placed under a platinum-boat containing sodium chloride, is heated by the ordinary flame, which keeps the sodium chloride in a state of semi-fusion, whilst the internal flame, produced by the oxygen passing up the small tube, impinges on the side, and at the same time somewhat under the boat; this causes the sodium chloride to volatilise, and at the same time the part of the flame passing up the side receives the sodium chloride vapour, and gives a very intense yellow light, which can be maintained for a long time.

DISCUSSION.

After referring to the fact that Dr. Perkin had this year been fifty years a Fellow of the Society, Prof. ARMSTRONG expressed the opinion that probably in days to come, when physicists understood sufficient chemistry to appreciate Dr. Perkin's work on magnetic rotation, it would be regarded as of greater importance even than his discovery of the coal-tar colours.

The PRESIDENT, in moving a vote of thanks to Dr. Perkin, congratulated him on having brought to its present state of perfection the beautiful method of exploring chemical constitution by an optical method which he had conceived twenty-five years ago, and which he had practically made his own. The apparatus described was unfortunately not an ordinary laboratory installation, and he was therefore afraid that Dr. Perkin was likely to bring more work upon himself, since the discoverers of new compounds would more and more have to depend on him for the determination of magnetic rotations when, as was certain to be the case, the value of the method became more widely recognised. The President reminded the meeting how largely the pages of the *Transactions* already bore testimony to the value of the method and to the courtesy of the author in placing his services at the disposal of investigators.

*68. "The Rusting of Iron." By GERALD TATTERSALL MOODY.

Contrary to the statement of Dunstan, Jowett, and Goulding (*Trans.*, 1905, lxxxvii., 1548), it is found that when bright iron is left in contact with air and water, both of which have been completely freed from carbonic acid, the metal remains untarnished, whatever the duration of the exposure. No absorption of atmospheric oxygen by iron takes place in presence of water, provided that carbonic acid has been first removed from both air and water, but on admission of a small quantity of the gas, rapid oxidation of the metal and diminution in volume of the oxygen are observed.

It is found, moreover, that the composition of iron rust is not fairly represented by the formula $\text{Fe}_2\text{O}_3(\text{OH})_2$, as stated by the foregoing investigators. An examination of a number of recently formed specimens shows that a large proportion of the iron is invariably present in the ferrous state, partly as oxide and partly as carbonate.

The explanation of rusting as a process involving the production of hydrogen peroxide, as advanced by Dunstan, is directly negated by experimental evidence, which shows that atmospheric corrosion results first from the interaction of iron and carbonic acid, whereby ferrous salt is formed, and subsequently from the more or less complete oxidation of ferrous salt by oxygen.

DISCUSSION.

Prof. ARMSTRONG said that, having seen the work, he was able to testify to the extreme care and patience which Dr. Moody had devoted to the inquiry; the experiments

had been made without bias, solely with the object of ascertaining whether iron was oxidisable by water and oxygen alone. The result was beyond question. It was not creditable to chemists, however, that problems of such fundamental importance should have so long been neglected in favour of work of no particular value to anyone, and that it should still be possible to dispute on such questions. Notwithstanding all the talk about ions, we were still without any clear accepted doctrine as to the conditions which determined the attack of oxygen on metals. Personally he had never been in doubt since he had realised that all such actions were essentially electrolytic—he had therefore felt unable to believe in the possibility of the interaction of iron, oxygen, and water taking place in the absence of an electrolyte—water not being an electrolyte. He had also never been able to accept the peroxide explanation; even supposing that rusting were inhibited by all substances which decomposed the peroxide, there was no reason to suppose that the destruction of the peroxide could in any way prevent the oxidation of the metal; some other explanation must be sought for the stoppage of action.

Mr. A. R. LING recounted his experiences with an acid water, derived from the red sandstone of Somersetshire, which vigorously attacked iron, producing rust. This action was prevented by adding to the water 7 grains per gallon of lime, but an equivalent amount of sodium carbonate was without effect. Caustic alkalis in equivalent amount prevented rusting only so long as the water was kept out of contact with the atmosphere. Rusting occurred also in presence of alkali sulphites.

Dr. GOULDING pointed out that the hydrogen peroxide solutions employed in Dunstan, Jowett, and Goulding's experiments did not contain free mineral acid, as Dr. Moody had stated, but were purified in all cases. The method usually adopted was to shake the solution thoroughly with barium carbonate, and afterwards to boil it under reduced pressure in order to eliminate carbon dioxide.

Mr. W. A. DAVIS referred to the opinion expressed by Prof. Dunstan and his colleagues in their paper, that Dr. Moody had "misread" the account given by Giorgis (*Gazzetta*, 1891, xxi., 510) of the action of hydrogen peroxide on magnesium. The tenor of this paper is to show that hydrogen peroxide when freed as far as possible from carbon dioxide attacks magnesium very much less readily than ordinary hydrogen peroxide containing carbon dioxide. Dr. Moody's statement that "hydrogen peroxide when carefully freed from carbon dioxide is *practically without action* on magnesium," is but a paraphrase of Giorgis' own conclusion that pure magnesium "*è ossidato in minima quantità dall'acqua ossigenata neutra*." Giorgis' hydrogen peroxide was not strictly neutral, but very slightly acid (*appena acida*), a fact which perhaps accounts for there being any action at all.

Dr. H. BORNS said that Dr. Moody had certainly taken great pains to settle the problem definitively, but he should however, have prevented the possibility of access of ozone, nitrogen compounds, sulphurous acid, &c., when finally admitting the air.

Dr. MOODY, in reply, said that the method of purifying hydrogen peroxide, as detailed by Dr. Goulding, was obviously inadequate, since in removing one impurity others were introduced. He doubted if acid could be completely removed by such a process without decomposing the whole of the hydrogen peroxide in the solution. With regard to Dr. Borns' remark, the arrangements for scrubbing the air were such that all acid constituents likely to attack iron were eliminated.

*69. "The Estimation of Carbon in Soils." By ALFRED DANIEL HALL, NORMAN HARRY JOHN MILLER, and NUMA MARMU.

Wet combustion with chromic acid has been frequently used for the estimation of carbon in soils, but, as Warrington has pointed out, it always gives results too low by 10–20 per cent. This is due to the oxidation of the carbon com-

pounds not proceeding so far as carbon dioxide, and is shown by the authors to be obviated by the introduction of a short length of red-hot copper oxide between the reacting flask and the alkali used for absorbing the carbon dioxide. The authors employ a Reiset tower for absorbing the carbon dioxide, which is then estimated by double titration, as suggested by Brown and Escombe.

DISCUSSION.

Dr. VOELCKER thought the process described would be a good one, and it had the advantage that both the carbonic acid and the organic carbon could be estimated in the one portion of soil. It would be interesting to know whether the authors had made a comparative test by Pettit and Schaub's method (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1640), which consisted in combustion with sodium peroxide.

70. "Electrolysis of Salts of $\beta\beta'$ -Dimethylglutaric Acid." By JAMES WALKER and JOHN KERFOOT WOOD.

Sodium ethyl $\beta\beta'$ -dimethylglutarate, when electrolysed in concentrated aqueous solution, yields as chief product the diethyl ester of $\beta\beta\beta'\beta'$ -tetramethylsuberic acid. This ester, the corresponding acid, and some of its salts are described.

Sodium $\beta\beta'$ -dimethylglutarate under like conditions yields at the anode chiefly carbon monoxide and carbon dioxide. There is formed simultaneously, however, a small quantity of a pentene, C_5H_{10} , which was proved to be unsymmetrical methylethylethylene. The formation of this compound can only be explained on the assumption of the migration of a methyl group. This affords an analogue to the production of ethyl isolauronolate on the electrolysis of sodium orthoethylcamphorate.

71. "Bromo- and Hydroxy-derivatives of $\beta\beta\beta'\beta'$ -Tetramethylsuberic Acid." By JOHN KERFOOT WOOD.

Perkin and Thorpe (*Trans.*, 1899, lxxv., 48) found that the bromo-esters of $\beta\beta\beta'\beta'$ -dimethylglutaric acid when heated with alcoholic potash, lose hydrogen bromide, and are converted into the caronic acids. The author has investigated the action of alcoholic potash on the bromo-derivatives of $\beta\beta\beta'\beta'$ -tetramethylsuberic acid, the ester of which is the direct synthetical product obtained during the electrolysis of sodium ethyl $\beta\beta'$ -dimethylglutarate. The action in this case is of a different nature from that investigated by Perkin and Thorpe; no cyclic compounds were formed, the only products isolated being hydroxy-derivatives of $\beta\beta\beta'\beta'$ -tetramethylsuberic acid.

72. "Some New *o*-Xylene Derivatives." By GEORGE STALLARD.

A new bromo-*o*-xylene ($CH_3:CH_3:Br = 1:2:3$) is obtained by hydrolysis of a bromosulphonic acid obtained by Kelbe by brominating *o*-xylene-4-sulphonic acid.

On sulphonation, it gives a mixture of two acids, one of which, the major product, has its substituents in the following positions:— $CH_3:CH_3:Br:SO_3H = 1:2:3:6$, as on debromination the *o*-xylene-3-sulphonic acid is obtained from it. The substituents of the other acid are present in the positions $CH_3:CH_3:Br:SO_3H = 1:2:3:4$ or $1:2:3:5$, as the compound is identical with Kelbe's acid mentioned above, and isomeric with the acid $CH_3:CH_3:Br:SO_3H = 1:2:4:5$, obtained by Jacobsen by sulphonating 4-bromo-*o*-xylene.

73. "A New Solvent for Gold." (Preliminary Note). By JAMES MOIR.

The author finds that gold-leaf dissolves fairly readily when floated on an acid solution of ordinary thiocarbamide. The action is rapid when a suitable oxidising agent is added; for example, when a solution of thiocarbimide is acidified and treated with a little ferric chloride, potassium dichromate, or hydrogen peroxide, the mixture dissolves gold-leaf after less than a minute's shaking. The solution

is not precipitated either by ferrous sulphate or by stannous chloride (except after long standing), whence it follows that the gold is present in solution as part of a complex ion. The gold compound has been isolated in brilliant, colourless, six-sided lozenges, striated parallel to the longest axis, and is identical with a compound which the author has obtained by boiling a mixture of sodium aurichloride and thiocarbamide solutions. It is apparently different from the compound $AuCl_2 \cdot 2CH_4N_2S$, described by Emerson Reynolds and by B. Rathke as being obtained in the reaction between aurichloride and thiocarbamide, since the mean of four concordant analyses gave $Au = 45.42$, whereas $AuCl_2 \cdot 2CH_4N_2S$ requires 51.24 per cent. Both Reynolds and Rathke give the theoretical value for gold in this compound as about 51.05, owing to the use of an incorrect value for the atomic weight of gold.

74. "The Molecular Condition in Solution of Ferrous Oxalate." (A Correction). By SAMUEL EDWARD SHEPPARD and CHARLES EDWARD KENNETH MEES.

In a paper on this subject (*Trans.*, 1905, lxxxvii., 189), the authors found for the dissociation-constant $\frac{[Fe(C_2O_4)_2]'}{[C_2O_4]''}$

the value 0.81 at 20°. Abegg and Schäfer working at 25° find the value 0.37, a discrepancy too considerable to be due to the temperature difference. Prof. Abegg, who has very kindly brought this circumstance to the authors' notice, has also pointed out the cause of this discrepancy. This was due to an error in the authors' calculation, whereby in calculating the concentration of $Fe(C_2O_4)_2''$ the permanganate titre for C_2O_4'' was added. The correct calculation is as follows:—The increase in the permanganate titre being 68.4 c.c., of this two-thirds are equal to 45.7 molecules of FeC_2O_4 dissolved. These 45.7 molecules of FeC_2O_4 , taking 45.7 molecules of C_2O_4'' from the 197.8 molecules of C_2O_4'' originally present, form 45.7 molecules of $Fe(C_2O_4)_2''$ and leave $197.8 - 45.7 = 152.1$ molecules C_2O_4'' , so that $K = \frac{45.7}{152.1} = 0.30$.

From the accepted results with longer time of stirring, the re-calculated value for K is 0.39 at 20°, in good agreement with Abegg and Schäfer's value 0.37 at 25° (*Zeit. Anorg. Chem.*, 1905, xlv., 317).

75. "Acetyl and Benzoyl Derivatives of Phthalimide and Phthalamic Acid." By ARTHUR WALSH TITHERLEY and WILLIAM LONGTON HICKS.

Phthalic anhydride, like succinic anhydride (*Trans.*, 1904, lxxxv., 1679), interacts with sodium benzamide, as well as sodium acetamide, yielding the corresponding acylphthalamic acids, $CO_2H \cdot C_6H_4 \cdot CO \cdot NH \cdot COR$. The latter readily undergo internal condensation on treatment with acetyl chloride, giving the acylphthalimides, $C_6H_4 \cdot \begin{smallmatrix} CO \\ < \\ CO \end{smallmatrix} > N \cdot COR$, identical with products obtained by the acylation of phthalimide, namely, benzoylphthalimide by pyridine benzoylation and acetylphthalimide, which has already been described by Aschan (*Ber.*, 1886, xix., 1400), by heating phthalimide with acetic anhydride.

Both acylphthalimides decompose on cautiously warming with aqueous sodium carbonate, the imide ring undergoing hydrolytic rupture with formation of the corresponding acylphthalamic acid $CO_2H \cdot C_6H_4 \cdot CO \cdot NH \cdot COR$. Aschan, on the other hand, stated that acetylphthalimide was hydrolysed with alkalis, giving phthalimide and acetic acid. The authors cannot confirm this observation, but show that when hydrolysis occurs it is preceded by rupture of the cyclic imido-grouping. Similar observations have been made by one of the authors (*Trans.*, 1904, lxxxv., 1686) in the case of benzoylsuccinimide, which on hydrolysis first yields benzoylsuccinamic acid, and finally succinic and benzoic acids and ammonia.

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, April 2nd, 1906.

Mr. A. G. SALAMON in the Chair.

"*Ropiness in Flour and Bread: its Detection and Prevention.*" By E. J. WATKINS.

Breads most frequently attacked by this disease are such as contain bran or low-grade white flours.

In the present investigation it has been sought, by means of culture experiments and the artificial production of ropiness in sound flour, to establish the identity of an organism isolated from specimens of ropy bread and flour obtained in England.

Cultures made from this bread yielded a small motile bacillus, which, after repeated sub-culturing, was used in a series of experiments made with a known sound flour. Varying proportions of the culture were added to the water used for making dough. Such doughs when fermented showed no sign of bacterial effects, and the bread produced was of normal character when it left the oven. The bread, when kept in a moist atmosphere at temperatures of 30—35° C., became ropy in about twenty-four hours; when the temperature was kept below 18° C., the disease did not appear. Dryness of the air generally prevented ropiness, even when the temperature was high.

Acids exercise a powerful influence in preventing the growth of the bacillus; it being found, in a series of tests with varying quantities of acetic acid in the dough, that the bread did not become ropy when kept long periods under conditions suitable to the bacillus.

The cultural and microscopic characters prove the organism to be *Bacillus Mesentericus* (Flügge).

Bakers have been held responsible for the appearance of rope in their bread, but there is good reason for the view that flour is the medium conveying the bacillus or its spores.

The great heat-resisting power of the spores of this bacillus prevents the sterilisation of the bread by baking. Flour which has been found to contain the bacillus should be held over until the cold season and then worked up with addition of a small amount of acetic acid to the dough; no fear need then be entertained of the bread being attacked during storage.

"*The Röse-Herzfeld and Sulphuric Acid Methods for the Determination of the Higher Alcohols.*" (A Criticism). By V. H. VELEY, F.R.S.

The two methods generally adopted for the determination of the higher alcohols are the Röse-Herzfeld (officially recognised in this country, Germany, and Switzerland) and the sulphuric acid method adopted in France, consequently practised in this country, and officially used as a general qualitative test for the purity of all kinds of alcohol in Russia.

Since these methods give very divergent results in the hands of different analysts, the author records various experiments to determine the accuracy or otherwise of the processes, and also criticises them.

NOTICES OF BOOKS.

The Gases of the Atmosphere. By Sir WILLIAM RAMSAY, K.C.B., F.R.S. Third Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1905.

THIS version of the "tale of the air," written by one who has done much to unfold it, will be read with interest by the general reader who has had no special scientific training, and it will arouse enthusiasm to read here of the early experimenters, their successes and failures, and their blind guesses after truth, all of which Sir William Ramsay

describes graphically, giving interesting extracts from the works of the early chemists who occupied themselves with the study of the air. Then the author passes to the discovery of argon and the investigation of its properties, followed by the other inactive gases, while to the third edition a chapter has been added on the radio-active gases (the emanations), in which a short and concise account is given of the discovery of radio-activity, its detection, and the law of decay, which is discussed exceptionally clearly. The investigation of the properties and behaviour of the emanations, as far as we now know them, brings to an end a book every page of which is full of interest for the chemist as well as the general reader.

Über die Vorgeschichte und die Anfänge der Chemie. ("The Early History and the Beginnings of Chemistry"). By Dr. FRANZ STRUNZ. Leipzig and Wien: Franz Deuticke. 1906.

THIS short introduction to the history of the chemistry of antiquity bears evidence of painstaking work on the part of its author, who has selected his material with the utmost care. Though only very short (it could easily be read through from beginning to end in an hour), it is full of interesting information. Only the most important of the developments of early chemistry are to be found in the book, and the subject is treated more especially from the point of view of the practice of the ancients chiefly as regards metallurgical operations. Thus, while the earliest methods of extracting the better known metals from their ores are fully discussed, we find no accounts of the manufacture of glass and soap. The introduction summarises such theoretical views on the composition of substances as were current among the older philosophers, and this chapter is particularly interesting and brightly written.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 13, March 26, 1906.

Isolation of Dysprosium, and its chief Atomic Characteristics.—G. Urbain.—The author isolates about 50 grms. of an earth which presents the characteristic spectrum of dysprosium. Four consecutive fractions have the same mean atomic weight, 162.49. The oxide is white, and does not change to peroxide when calcined in oxygen. The salts have a yellowish green coloration. The chief characteristics of the dysprosium compounds, such as solubility of salts, basicity of oxide, &c., place this element in the series of the rare earths between terbium and the new holmium. Outside the visible absorption spectrum, dysprosium presents a particularly sharp ultra-violet spectrum, composed of intense diffused bands. The whole spectrum contains the following lines, a neutral solution of chloride being used.

	λ.	
400	to 394	Weak; very diffused.
392	" 384.5	Very strong; diffused.
381.5	" 377	Maximum 379.5.
368.5	" 361.5	Very strong; diffused; maximum 365.
355.5	" 345.5	Extremely strong and diffused; max. 351.
340	" 336	Strong; diffused; maximum 338.
329	" 316	Extremely strong; maximum 322.5.

The Action of Xantic Leucomains on Copper.—N. Slomnesco.—Theobromine, theophiline, urea, and probably also the other xantic leucomains have the property of precipitating copper from its solution in the form of the yellow hydrate. The action is not only a

simple reduction but consists also of a tendency for the bases to combine with the copper. If copper is boiled with these bases in aqueous solution the same characteristic precipitate is produced, which has a dirty yellow colour.

A New Type of Equilibrium Reaction.—L. J. Simon.—The author makes a series of experiments on the equilibrium between pyruvic acid and urethane in the absence of all condensation agents. He also suspends a known weight of pyruvic acid in a definite volume of water. This rapidly dissolves when the temperature is raised. On cooling, the dissociation is measured. He finds:—1. That for a definite concentration the state of the solution depends on the temperature to which it has been carried. The dissociation increases with the temperature. 2. The dissociation increases with the concentration, on account of the higher temperature which must be attained to ensure solution in the same time. 3. The dissociation is total for the greatest concentrations. For weak solutions there seems to be one molecule dissolved to one dissociated.

Estimation of Cadmium.—H. Baubigny.—In a previous research the author proved that cadmium sulphide is not as easily decomposed as has hitherto been supposed. Under certain conditions, which the author describes in detail in the present paper, the filter-paper containing the sulphide precipitate can be burnt in the ordinary way.

Estimation of the Albumenoid Matter in Milk.—MM. Trillat and Sauton.—The authors describe a method by which (1) all the albumenoid matter can be separated from milk; (2) it can be shown to possess the elementary composition of casein; (3) it can be shown that there is no variation in weight.

MISCELLANEOUS.

Effects of Blows upon Chemical Elements, especially the Light Metals.—O. Ohmann.—1. *Calcium.*—Doerner (*Berichte*, 1906, xxxix., 211) has already described the phenomenon which occurs when electrolytic calcium is struck upon an anvil, but he observes that the explosibility is much smaller if no iron oxide or rust is present. The author, however, finds that sparks appear when the metal is struck between two pieces of quartz and of granite. He believes that a partial vaporisation of calcium takes place at the place where the pressure is greatest, and it combines with oxygen. This view is confirmed by the following facts:—(a) A brighter light is produced when the experiment is performed in an atmosphere of oxygen; (b) if the metal is struck with the edge of the hammer the sparks appear, but if the hammer is rounded, or the material is not very hard, only a faint light is seen; (c) if a sharp blow is struck with the whole surface of the hammer an explosion occurs; this appears to be an explosion more in a physical than in a chemical sense; (d) if heat has accumulated in consequence of many unsuccessful blows, sometimes after a comparatively gentle blow an intense light appears, and an explosion occurs. 2. *Sodium.*—A clear luminescence appears when a piece of sodium as big as a pea is struck with a hammer. 3. *Potassium.*—With potassium a vigorous action occurs at each blow; with very moderate blows violet flames strike out on all sides, and clouds of vapour with a piercing odour are formed. If it is struck more sharply, glowing balls are projected to some distance. 4. *Lithium.*—A very small piece of lithium after a few blows gives with each subsequent blow a bright flame often accompanied by an explosion. The flame is sometimes red or white and dazzling (especially when the blows are hard). Besides these flames small sparks appear, very much like the sparks obtained from iron. 5. *Aluminium.*—Only very small sparks were obtained when the powdered metal was struck, and sometimes no phenomena at all occurred. Electrolytic

barium would probably exhibit the phenomenon, but it does not appear with barium obtained from amalgam. Thallium gave no result. 6. *Phosphorus.*—When a few c.m. were struck a doughy plate was formed, from which sparks were obtained.—*Berichte*, xxxix., No. 4.

MEETINGS FOR THE WEEK.

MONDAY, 30th.—Society of Arts, 8. (Cantor Lectures). "Ivory in Commerce and in the Arts," by Alfred Maskell.

TUESDAY, May 1st.—Royal Institution, 5. "Greek Classical Dress in Life and in Art," by Prof. G. Baldwin Brown, M.A.

--- Royal Institution, 5. (Annual Meeting).

--- Society of Arts, 4.30. "Social Conditions in Australia," by the Hon. J. G. Jenkins.

WEDNESDAY, 2nd.—Society of Arts, 8. "Submarine Signalling," by J. B. Millet.

--- Society of Public Analysts, 8. "Estimation of Fat in Homogenised Milk," by H. Droop Richmond. "Milk Analysis," by H. Droop Richmond and E. H. Miller. "Composition of Seifon," by A. E. Parkes. "The Polenske Method for the Detection of Coconut Oil in Butter," by S. Rideal and H. G. Harrison. "Presence and Detection of Cyanogen in Java and other Beans," by R. K. Talbot and K. T. Thomson. "Examination of Linseed, Olive, and other Oils," by R. T. Thomson and H. Dunlop.

THURSDAY, 3rd.—Royal Institution, 5. "The Digestive Tract in Birds and Mammals," by Dr. P. Chalmers Mitchell, M.A.

--- Chemical, 8.30. "Relation between Absorption Spectra and Chemical Constitution—Part V., The Isonitroso-compounds," by E. C. C. Baly, E. G. Marsden, and A. W. Stewart. "Action of Tribromopropane on the Sium Derivative of Ethyl Malonate" (Part II.), by W. H. Perkin, jun., and J. L. Simonsen. "Brazilin and Hæmatoxylin—Part VII., Some Derivatives of Brazilein," by P. Engels and W. H. Perkin, jun. "Pipitzaic Acid," by J. M. Sanders. "Constitution of the Hydroxides and Cyanides obtained from Acridine, Methyl-acridine, and Phenanthridine Methiodides," C. K. Tinkler. "Constitution of Ammonium Amalgam," by E. M. Rich and M. W. Travers. "Action of Light on Potassium Ferrocyanide," by G. W. A. Foster.

FRIDAY, 4th.—Royal Institution, 9. "The Steam Turbine on Land and at Sea," by the Hon. Charles A. Parsons, C.B., F.R.S., &c.

SATURDAY, 5th.—Royal Institution, 3. "English Furniture in the Eighteenth Century," by Prof. Charles Waldstein, Ph.D., &c.

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Mdme. CURIE'S Thesis

ON

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A MODIFIED EVOLUTION METHOD FOR THE DETERMINATION OF SULPHUR IN PIG-IRON.

By J. McFARLANE and A. W. GREGORY.

It is well known that only part of the sulphur in pig-iron is evolved as hydrogen sulphide by the action of hydrochloric or sulphuric acid. Pig-irons containing a considerable proportion of combined carbon (mottled and white irons, and the shots obtained by pouring the molten metal into water), when acted on by hydrochloric acid, give only a part of their sulphur as hydrogen sulphide—the proportion varying very considerably, and methods of sulphur determination based on this reaction are unreliable.

This difficulty is partially overcome by annealing the powdered sample at a bright red heat in an inert atmosphere (Walters and Miller, *Journ. Iron. and Steel Inst.*, 1902, No. 1, p. 851). If, however, the powdered pig-iron be mixed with a little cream of tartar and heated to redness in a covered crucible for some time, the whole of the sulphur may be evolved as hydrogen sulphide by the action of hydrochloric acid, and the sulphur estimated by the oxidation of this compound. The exact method of working which we have adopted is as follows:—

Five grms. of the powdered sample are taken and mixed intimately with about 0.5 gm. of cream of tartar, the mixture wrapped in filter-paper and placed in a small crucible. The crucible is covered and heated to bright redness in a muffle for a quarter of an hour, after which it is removed and allowed to cool. The resulting mass is powdered by gentle crushing in a glass mortar and transferred to the evolution flask, the delivery tube of which dips into an ammoniacal cadmium chloride solution. Boiling hydrochloric acid (2 parts acid to one part water) is then introduced into the evolution flask. When the reaction has become quiescent, the liquid in the flask is boiled to expel hydrogen sulphide from solution.

The sulphur is now in the form of cadmium sulphide. The liquid containing this in suspension is acidified with hydrochloric acid, and the hydrogen sulphide in solution immediately titrated with standard iodine solution, in the same manner as in the estimation of sulphur in steel by the cadmium chloride method.

The cadmium chloride solution is prepared by dissolving 20 grms. of cadmium chloride in a litre of water and adding a litre of strong ammonia.

For each estimation, 25 c.c. of this solution is diluted with about 300 c.c. of water and placed in a tall beaker. The iodine solution, each c.c. of which is equivalent to 0.00025 gm. of sulphur, is standardised by means of a steel of known sulphur content. As a check on our results, a series of pig-irons was taken and the sulphur in each accurately determined by the "aqua regia" method and also by the evolution process given above.

In order to ensure great accuracy in the aqua regia method, we proceeded as follows:—2½ grms. and 7½ grms. of the sample were separately dissolved in 70 c.c. of a mixture of hydrochloric and nitric acids (100 c.c. HNO₃ and 50 c.c. HCl) to which a few grms. of potassium chlorate had been added. Each was evaporated carefully to dryness and roasted, allowed to cool, taken up in 40 c.c. hydrochloric acid, evaporated to dryness again to expel nitric acid, dissolved in 50 c.c. hydrochloric acid, boiled to low bulk, diluted, and filtered.

The filtrates were diluted with 400 c.c. of distilled water, boiled, and precipitated with 50 c.c. of 20 per cent solution of barium chloride. The solutions were allowed to stand over night on a warm plate.

The barium sulphate precipitate was filtered off, washed with very dilute boiling barium chloride solution containing a little hydrochloric acid to remove the last traces of iron. Finally, the barium sulphate was washed with boiling distilled water, ignited, and weighed. The difference between the weight of barium sulphate obtained from the 7.5 grms. and the 2.5 grms. of pig-iron gave the true weight of barium sulphate derived from 5 grms.; errors due to the reagents used containing sulphur being thus eliminated. The following results were obtained by the two methods:—

	Aqua regia method.		Evolution method.	
	Per cent S.		Per cent S.	
1.	—	0.093	0.090	0.089
2.	0.090	0.090	0.091	0.094
3.	0.096	0.098	0.093	0.095
4.	0.066	0.066	0.066	0.068
5.	0.078	0.080	0.080	0.080
6.	0.060	0.060	0.060	0.061
7.	0.063	0.063	0.062	0.061
8.	—	0.076	0.078	0.078
9.	0.069	0.068	0.069	0.070
10.	—	0.082	0.080	0.080

The above results were obtained with samples broken from ordinary pigs. Equally good results were obtained with "chilled shot" samples as follows:—

	Aqua regia method.		Evolution method.	
	Per cent S.		Per cent S.	
1.	0.186	0.188	0.190	—
2.	0.197	0.204	—	—
3.	0.129	0.129	—	—
4.	0.115	0.113	—	—
5.	0.086	0.085	0.087	—
6.	0.148	0.152	—	—
7.	0.222	0.222	—	—

The following results were obtained with "chilled" samples containing a very high percentage of sulphur:—

	Aqua regia method.		Evolution method.	
	Per cent S.		Per cent S.	
1.	0.448	0.440	0.438	—
1.	0.292	0.285	0.282	—
3.	0.390	0.402	0.406	—
4.	0.476	0.458	0.464	—

The cream of tartar used should be free from sulphur (usually present as sulphates).

No elaborate absorption vessel is required, since the hydrogen sulphide is completely absorbed by allowing the evolved gases to bubble through the cadmium chloride solution contained in a beaker.

The efficiency of this apparently crude method of absorption was shown by the following experiment:—

A pig containing over 0.6 per cent of sulphur was dissolved in the evolution flask, a very rapid evolution being maintained. The evolved gases were passed through two small flasks containing the diluted ammoniacal cadmium chloride solution, first passing through No. 1 flask and then through No. 2.

There was no trace of a precipitate in No. 2 flask, and, after its contents were acidified, only 0.5 c.c. of the standard iodine solution was required to oxidise the hydrogen sulphide absorbed, equivalent to 0.00013 gm. of sulphur. The drillings or powdered pig-iron should be in a fine state of division, so that the evolution of gas may be as rapid as possible.

Technical College, Finsbury, Old Students' Association.—A Meeting of Old Students, at which Sir Owen Roberts has kindly consented to preside, will be held at the Technical College, Finsbury, on May 8th, at 8 p.m. Any old student who has not received a notice of this meeting is requested to communicate with J. W. G. Brooker, Durlstone, Brockley Park, Forest Hill, S.E.

A REVISION OF THE ATOMIC WEIGHTS OF
SODIUM AND CHLORINE.*By THEODORE WILLIAM RICHARDS
and
ROGER CLARK WELLS.

(Continued from p. 195).

THE SOLUBILITY OF ARGENTIC CHLORIDE.

MULDER pointed out in 1857 that the solubility of argentic chloride is sufficient to affect all quantitative results into which the precipitation of this substance enters ("Die Silber-Probirmethode, Leipzig, 1859). Stas overlooked this solubility in his early determinations, and hence in 1876 repeated some of them ("Oeuvres," i., 751). Other more recent experimenters have in general confirmed Stas's later conclusions about this solubility, so that it is not important here to give a lengthy statement of our further confirmatory results. (For references see Böttger, *Zeit. Phys. Chem.*, 1903, xlv., 189; Richards, *Proc. Am. Acad.* 1893, xxix., 69).

There can be no doubt that freshly precipitated argentic chloride is soluble in cold water to the extent of several m.grms. per litre, and that this solubility steadily diminishes, without a very sharp change at any time, as the precipitate remains in contact with the liquid.

A variable solubility of this nature may be due to one of two causes. Either the precipitate is capable of assuming two or more allotropic forms, of which the least stable appears at first (Ostwald, *Zeit. Phys. Chem.*, 1897, xxii., 307), or else it separates in a finely divided state, and gradually becomes aggregated into larger masses. The work of Ostwald (*Zeit. Phys. Chem.*, 1900, xxiv., 495) and of Hulett (*Zeit. Phys. Chem.*, 1901, xxxvii., 385; 1904, xlvii., 357) has shown how greatly a difference in size of the grains may affect the solubility, especially of a salt only slightly soluble.

The latter explanation seems the more probable for several reasons. In the first place, no sharp change in the solubility has ever been detected, such as would be expected from the appearance of a new more stable solid phase. Again, the difference between the specific gravity of the flocculent precipitate and fused horn-silver is very slight, and their heats of solution in cyanide are identical, indicating little or no difference of molecular constitution between the two. (Lævinsohn determined the specific gravities; his results were verified and the thermo-chemical argument added to them by Dr. W. N. Stull and one of us, in some work not yet published). Moreover, as will be shown later, the curdy precipitate may be successfully washed in a measure unattainable with crystalline powders, showing that the innermost recesses of the solid are more than usually accessible, and therefore that the structure is very finely divided and loosely knit. The more compact, less soluble precipitate, obtained either by heating or by long standing, has largely lost this possibility of being thoroughly washed, and has become also much less soluble—facts which are quite in line with the above hypothesis. However this may be, the uncertainty of the solubility is a fact of important significance to the analyst, for it obliges him to determine the amount of solution in every experiment—the solubility can never be assumed as known.

The matter is yet further complicated by the well-known fact that the presence of excess of either ionised silver or ionised chlorine causes a depression of the solubility, in the manner demanded by the law of concentration effect (Hoitsema, *Zeit. Phys. Chem.*, 1896, xx., 272). A large excess of either precipitant reduces the solubility to so small a value as to be practically negligible in most cases (see below). This may indeed be the reason why the precipitate appears in a form so loosely knit, for at the moment of precipitation it is almost impossible that the two precipitating liquids should for more than an instant be exactly equivalent. Hence each first particle of precipitate would

quickly be surrounded by a liquid unfavourable to its union with another in compact crystalline fashion.

Mulder thought that an excess of either silver or chloride equivalent to four times the weight of the dissolved argentic chloride was enough to complete the precipitation, and Stas thought that exactly three times the equivalent amount sufficed. It is clear now that this limit is determined merely by the efficiency of the means used to detect the last faint cloud of precipitate, and then only approximately.

As has been said, the changing solubility demands that every filtrate be tested quantitatively. The methods which may be used are all open to some criticism. The determination of electrolytic conductivity is in vain when any other electrolyte is present, and its interpretation is complicated even in pure aqueous solution by possible hydrolytic complications. The determination of electromotive force depends upon the rigorous application of the law of concentration effect to electrolytes—a somewhat doubtful question. The actual evaporation of the solution and weighing of the precipitate leads to many errors when silver is in excess (Richards, *Proc. Am. Acad.*, 1893, xxix., 71), and the determination of the intensity of the opalescence upon precipitating the dissolved chloride depends greatly on the details of the production of the opalescence.

From among all these methods we chose the last, after a very carefully study of their probable errors. But although fairly confident of its results, for reasons shortly to be given, we were careful in every case to allow in each experiment as little dissolved argentic chloride as possible, so as to reduce the possible error to a minimum.

The method of comparing the intensity of the cloudiness of opalescent solutions, and therefore the quantities of suspended precipitate, has already been discussed at some length in a paper on the nephelometer (Richards and Wells, *Am. Chem. Journ.*, 1904, xxxi., 235). This instrument consists of a device for the comparison of the tint or brightness of two solutions containing precipitate, viewed against a dark background. By making one of these opalescent mixtures from a known amount of material, an unknown amount may be estimated by comparison with it. It is easy to show that with this instrument the average of many results is within 1 or 2 per cent of the truth, so that the error with 2 m.grms. of dissolved argentic chloride is probably less than 0.04 m.grm. This degree of accuracy is as great as can be obtained in the collection of a precipitate for weighing, hence the method is to be ranked among those suitable for exact work.

With the perfected nephelometer it was possible to study the progressing precipitation of very dilute argentic chloride in a way previously impossible, and several unexpected irregularities were found during its course. Since these are important in the quantitative sense, they must all be briefly discussed.

The most striking of these is the variation in the time of complete precipitation caused by the presence of electrolytes. For example, a solution of argentic chloride, on adding a slight excess of soluble argentic salt, becomes opalescent, far more quickly in the presence of much sodic nitrate or nitric acid than in the absence of such an electrolyte. At the end of five minutes the former solution appears about three times as cloudy as the latter; and several hours are needed for the two solutions to attain equality of opalescence at a maximum value, which thereafter remains constant. It appears from this fact that the precipitate probably at first forms in a colloidal state, since electrolytes are known to hasten the precipitation of colloids. This inference is confirmed by the occasional appearance of pale blue or pink tints in the incipient precipitate, which disappears as the cloudiness becomes more intense.

Oddly enough, a solution of pure argentic chloride (made by shaking the curdy precipitate with water and filtering) attains its maximum cloudiness after subsequent addition of argentic nitrate more rapidly than a solution of similar dilution made by mixing equivalent amounts of very dilute

* Published by the Carnegie Institution of Washington, April, 1905.

argentic nitrate and sodic chloride solutions. The trace of sodic nitrate left in the latter case seems to be unable to counteract some other tendency holding the precipitate in solution. At first it seemed possible that minute invisible "crystal germs" might be present in the filtered solution, which accelerated the appearance of the opalescence, but this surmise was soon overthrown experimentally. A solution made from curdy silver chloride and found nephelometrically to contain 1.28 m.grm. per litre, was diluted with an equal bulk of pure water, and its concentration after agitation for over one hour was determined by the nephelometer. The average concentration found by five trials, 0.61 m.grm. per litre, agree with that expected within a reasonable limit of error, and, moreover, the speed of precipitation was no less than before. There could hardly have been any "crystal germs" existing in the more dilute solution, hence one must assume that the undissociated part of the argentic chloride is really in a different state, when it is dissolved out of salt long formed from that in which it is when in the act of precipitation. The observation at least adds one more anomalous fact, perhaps giving a clue to some of the other anomalous facts, concerning the solubility of argentic chloride.

The application of these observations to the nephelometric analysis of a very dilute silver chloride solution is obvious. It is a difficult matter to prepare a standard which will behave in exactly the same way as the solution to be estimated. By adding appreciable quantities of nitric acid to each, it is nevertheless possible to hasten the precipitation of each so greatly as to cause them to proceed at a speed almost equal; and the maximum cloudiness thus quickly attained persists unchanged in relative intensity for hours. It seems highly probable that the result thus reached really represents the amount of dissolved argentic chloride; especially because the same result is attained after a much longer time even when no electrolyte is present.

The actual extent of the solubility of argentic chloride thus estimated varied through wide limits, as has already been stated. For the solution freshly filtered from the curdy precipitate in the usual condition at 20° the amount dissolved was ordinarily about 1.5 m.grms. per litre, a result about equal to that of Kohlrausch and Rose and others. On long standing such a solution was found to decrease in concentration, on one occasion to as little as 1.1 m.grm. per litre, although no visible precipitate was seen on the glass. The trace of material represented by this difference was probably adsorbed by the glass. This observation points out the necessity of determining the strength of an unknown solution immediately after its filtration, a precaution which was carefully heeded in the quantitative part of the work.

Although sodic nitrate and nitric acid hasten the precipitation of the curdy opaque form of argentic chloride, they augment slightly the amount which finally remains in solution. By means of the nephelometer it was found that a saturated solution of curdy argentic chloride in the presence of about tenth normal sodic nitrate and a small amount of nitric acid usually contained as much as 3 m.grms. of the slightly soluble halide per litre. A mixture of this type was present at the conclusion of each nephelometric experiment recorded in the experiment on the ratio between sodic chloride and silver, and the bearing of the actual value on the investigation will be there discussed.

The solubility of silver chloride in a liquid containing a large excess of one of its ions has been stated above to be "practically negligible in most cases." In determining the ratio between silver and silver chloride, however, it seemed advisable to determine even this solubility, which may partly represent the solubility of the undissociated silver chloride, as distinguished from that ionised, and also includes the slight correction for the imperfect retaining power of even the best filters. The fact that a single part of silver chloride may be detected in 30,000,000 parts of water by the nephelometer in the presence of an excess of

silver nitrate shows the approximate order of this solubility (Richards, *Proc. Am. Acad.*, 1893, xxix., 74).

In five experiments, in which silver chloride was precipitated by an excess of hydrochloric acid, the combined mother-liquor and wash waters remaining after filtration were evaporated to dryness. The residue was taken up with a very small quantity of ammonia, and then neutralised with nitric acid. After the addition of a slight amount of sodic chloride, the silver chloride was estimated by the nephelometer, by comparison with tubes made up with known amounts of silver in the same way.

Silver Chloride Found.

In 3 litres	0.09 m.grm. AgCl
In 3 litres	0.13 "
In 3 litres	0.05 "
In 2 litres	0.05 "
In 2 litres	0.05 "
Mean	0.03 m.grm. per litre

This value represents the solubility of argentic chloride in water containing sodic nitrate and an excess of hydrochloric acid, together with those traces of the substance which could not be collected upon a filter. It is not certain that the same value would be obtained if it were possible to determine this infinitesimal solubility in the presence of an excess of argentic nitrate; but the fact that the limiting value previously found by one of us is about of this order seems to render this probable. Hence, for the sake of completeness, the correction was applied to the results in the latter case as well as in the former, although it was so small as not even to affect the third decimal place of the atomic weight of sodium.

Further consideration of the solubility of argentic chloride will be given in other appropriate places.

(To be continued).

THIRTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1905.*

By F. W. CLARKE.

(Continued from p. 196).

Tellurium.

THE electro-chemical equivalent of tellurium has been determined by Gallo, in comparison with silver taken as $\text{Ag} = 107.93$ (*Atti Accad. Lincei*, [5], xiv., 33, 104; *Gazz. Chim. Ital.*, xxxv., 245). Three series of determinations are given, with weights reduced to a vacuum. The data are as follows:—

Weight Ag.	Weight Te.	Atomic weight Te.
0.74117	0.218412	127.22
1.03801	0.304514	126.65
0.91704	0.27256	128.30
1.041101	0.307117	127.35
1.09064	0.321952	127.42
1.16302	0.34582	128.16
0.968903	0.28646	127.64
1.518712	0.44767	127.28
0.906561	0.26836	127.76
0.995511	0.29586	128.28
0.86596	0.25656	127.90
1.11282	0.328318	127.44
Mean		127.617

Although these values are widely variable, the mean approaches closely to the atomic weight as determined by other investigators.

* From the *Journal of the American Chemical Society*, xxviii., No. 3.

Gutbier's re-determination of the atomic weight of tellurium is based upon the reduction of scrupulously purified tellurium dioxide by two distinct methods (*Ann.*, cccxlii., 266). In the first series of experiments the dioxide, mixed with finely-divided silver and quartz sand, was reduced by pure hydrogen. In the second series, hydrazine was the reducing agent. The data, with vacuum weights, are as follows:—

Weight TeO ₂ .	Weight Te.	Atomic weight.
<i>Hydrogen Series.</i>		
2.99688	2.39585	127.55
1.30740	1.04527	127.60
2.04325	1.63380	127.68
2.61725	2.09249	127.59
3.61725	2.89222	127.65
Mean		127.614
<i>Hydrazine Series.</i>		
1.90601	1.52390	127.62
1.03532	0.82784	127.67
2.2200	1.77480	127.55
Mean		127.613

Gutbier thus reaches the same value for tellurium as Gallo, which may be rounded off to 127.6; this is the value adopted in the International Table.

Bismuth.

In a Doctoral Dissertation by Lothar Birckenbach, some experiments are described involving the synthesis of bismuth trioxide from the metal, and also the reduction of the oxide to metal ("Ueber das Atomgewicht des Wismuths," Inaugural Dissertation, Erlangen, 1905). The bismuth was from several distinct sources, and included material received from Classen, whose determinations of this atomic weight were published several years ago.

In the first part of the research, bismuth was oxidised by means of nitric acid in porcelain crucibles. The oxide was tested for occluded gases, which were proved to be absent, or at least present in only insignificant traces. Three series of determinations are given, representing different samples of bismuth, with the subjoined results.

Weight Bi.	Weight Bi ₂ O ₃ .	Atomic weight.
{ 9.63289	10.74328	208.22
{ 10.41101	11.61288	208.04
{ 10.97914	12.24528	208.11
{ 10.1199	11.2880	208.10
{ 18.96770	21.15541	208.08
{ 11.99601	13.38001	208.01
{ 27.23022	30.37392	207.88
{ 24.9817	27.86431	207.99
{ 10.11284	11.27998	207.94
{ 28.35991	31.63053	208.10
Mean		208.05

By reduction of bismuth trioxide in a stream of ammonia gas, with precautions which are fully described in the original memoir, the following determinations were made.

Weight Bi ₂ O ₃ .	Weight Bi.	Atomic weight.
{ 1.45827	1.30751	208.14
{ 2.12432	1.90461	208.04
{ 3.0021	2.6918	207.92
{ 2.1012	1.8840	208.17
{ 3.0182	2.70620	208.16
{ 1.9091	1.71171	208.02
Mean		208.08

Birckenbach concludes, from all the determinations, that Bi = 208 approximately, and not 209 as measured by Classen.

The foregoing investigation was conducted under the direction of Gutbier, who has carried the work still further. In a preliminary notice, Gutbier states that eight analyses of bismuth bromide gave values for Bi ranging from 207.89 to 208.24, in mean 208.05 (*Zeit. Elektrochem.*, xi., 831). Additional determinations are being made.

Palladium.

In the elaborate memoir by Amberg (*Ann.*, cccxli., 235) on the atomic weight of palladium, several methods of determination are described; but all relate to analyses of palladosammine chloride, Pd(NH₃Cl)₂.

First, palladium was precipitated by electrolysis, and the chlorine in the remaining solution was weighed as AgCl. From the following data, the atomic weight A is determined by the proportion of Pd, B by the ratio between the original salt and AgCl.

Weight salt.	Weight Pd.	Weight AgCl.	A.	B.
1.06045	0.53609	—	107.38	—
1.00028	0.50528	1.35867	107.28	106.09
1.66386	0.84085	2.25437	107.33	106.59
0.83195	0.42092	1.12282	107.56	107.45
1.91591	0.96886	2.59799	107.44	106.45

In a second series of experiments the palladium was thrown down by hydrazine sulphate; in other respects this series is like the first.

Weight salt.	Per cent Pd.	Weight AgCl.	Atomic weight.
1.32423	50.12	1.78656	107.52
1.02642	50.29	1.39247	106.35
1.30335	50.36	1.76875	106.28
1.59709	—	2.16641	106.37
1.88622	50.49	2.55028	107.06
2.59665	50.68	3.51783	106.64

From the sum of all the chlorine determinations, Pd = 106.67 when Ag = 107.93, Cl = 35.45, N = 14.04, and H = 1.008. The weights are referred to a vacuum.

In the final series of determinations, palladium was electrolytically precipitated from a sulphuric acid solution of the palladosammine chloride with the aid of a rotating anode. Twelve analyses were made with three separate preparations of the chloride, and with the subjoined results:—

Weight salt.	Weight Pd.	Per cent Pd.	Atomic weight.
{ 0.62446	0.31470	50.396	106.70
{ 0.83878	0.42280	50.407	106.75
{ 1.50282	0.75725	50.389	106.67
{ 1.06704	0.53753	50.385	106.66
{ 1.98342	0.99971	50.403	106.74
{ 1.53093	0.77153	50.396	106.71
{ 1.18995	0.59971	50.398	106.71
{ 0.62635	0.31572	50.406	106.75
{ 1.76110	0.88739	50.388	106.67
{ 3.79639	1.91298	50.389	106.68
{ 3.97553	2.00333	50.392	106.69
{ 4.62100	2.32834	50.386	106.66

Sum 23.51777 11.85109 Mean .. 106.699

From the sums of the weights, Pd = 106.688. The probable value, derived from all the data, is put by Amberg at 106.7. If re-calculated with the new values for N and Cl, 14.01 and 35.473, the figure for palladium will be changed very slightly. The changes due to N and Cl respectively are in opposite directions, and nearly compensate each other.

Thorium.

R. J. Meyer and A. Gumperz (*Ber.*, xxxviii., 817) have investigated the supposed complexity of thorium, and have failed to confirm the results announced by Baskerville. First, about 700 grms. of thorium nitrate were separated into seven fractions by precipitation with potassium

chromate. The fractions were converted into the octohydrated sulphate, which was then applied to the atomic weight determinations. It was weighed first as hydrate, then as anhydrous salt after heating to 400°, and finally ignited to oxide. The data thus obtained are as follows:—

Fraction.	Wt. hydrate.	Wt. Th(SO ₄) ₂ .	Wt. ThO ₂ .	At. wt.
I.	1.2463	0.9301	0.5793	232.4
I.	1.3261	0.9927	0.6184	232.5
IV.	1.3910	1.0344	0.6442	232.3
V.	1.2543	0.9349	0.5821	232.2
VII.	0.8934	0.6680	0.4160	232.3
VII.	—	0.4296	0.2676	232.5

Secondly, thorium tetrachloride was fractionally sublimed in a stream of chlorine, and divided into three portions, namely—(1) the most volatile portion, “berzelium”; (2) the medium portion, “new thorium”; (3) the unsublimed residue, “carolinium.” These, converted into sulphate, gave the subjoined data.

Fraction.	Wt. hydrate.	Wt. Th(SO ₄) ₂ .	Wt. ThO ₂ .	At. wt.
1.	1.2573	0.9199	0.5730	232.5
1.	1.0424	0.7647	0.4764	232.6
2.	—	1.0650	0.6635	232.4
2.	1.0387	0.7758	0.4834	232.7
3.	1.1904	0.8824	0.5496	232.4
3.	0.7487	0.5545	0.3454	232.4

The mean of all is Th=232.43. No evidence of a breaking up of thorium was observed, and a spectroscopic examination of the products by Eberhard led to the same conclusion (*Ber.*, xxxviii., 826). A brief reply to Meyer and Gumperz was published by Baskerville (*Ber.*, xxxviii., 1444), in which he urged the importance of observing the exact conditions of his experiments—conditions from which his critics seem to have departed.

The radio-thorium described by Ramsay (*Journ. Chim. Phys.*, iii., 617) and Hahn (*CHEMICAL NEWS*, xci., 193; xcii., 251; *Ber.*, xxxviii., 3371; see also Sackur, *Ber.*, xxxviii., 1756) should be taken into account in any discussion of the atomic weight of thorium. It was extracted in very small amount from thorianite, and gave about 700,000 times as much emanation as an equal weight of ordinary thorium. Its atomic weight remains to be determined.

(To be continued).

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

PART II.—ANALYSIS OF THE TUNGSTEN GROUP.

By ARTHUR A. NOYES.

(Continued from p. 192).

Procedure and Notes (continued).

Procedure 39.—Combine the filtrate from the (NH₄)₂S precipitate (P. 35) with that from the Na₂CO₃ and S fusion (P. 38). Make the solution distinctly acid with H₂SO₄ (1.20), shake, and filter, using suction if the precipitate is large. (Precipitate, if its colour is that of precipitated sulphur, reject; if not, P. 41. Filtrate, if a sulphide has been precipitated from it or if it is at all yellow, or if it contains phosphate, P. 40; otherwise, reject).

Note.

1. Molybdenum, tin, and tungsten, when present in the H₂SO₄ precipitate, even in quantity as small as can be detected by the subsequent tests for these elements, impart either a dark colour or a deep yellow colour to that precipitate. Therefore, if the precipitate has the colour of pure sulphur, it is not necessary to examine it

further. In a doubtful case, the precipitate should be ignited as described in P. 41, and the amount of the residue estimated or weighed. Molybdenum is completely or nearly completely precipitated by the H₂SO₄, and tin is completely precipitated by it. Tungsten, when present in large quantity, divides itself between the precipitate and filtrate; when present alone in small quantity it passes almost wholly into the filtrate, to which even a quantity of 1 m.grm. imparts a distinct yellow colour. In the presence of the other elements precipitated as sulphides, a small quantity of tungsten may, according to the conditions, either be completely precipitated with them, or it may pass entirely into the filtrate, and without imparting to it a yellow colour. If a precipitate of sulphide is obtained, it is therefore necessary to test the filtrate for tungsten by P. 40, even though it be colourless. In the presence of phosphate, too, even a considerable quantity of tungsten seems to pass completely into the filtrate.

Procedure 40.—If the filtrate from the H₂SO₄ precipitate (P. 39) requires examination (see P. 39), evaporate it till the residue becomes almost dry, transfer the latter to a platinum crucible, and ignite as long as H₂SO₄ fumes are expelled. Add to the residue a little HF and a few drops H₂SO₄, and again evaporate till fuming ceases. Add to the residue twice its volume of solid Na₂CO₃, and heat for five minutes over a powerful burner. Cool, fill the crucible with water, heat till the mass is dissolved, and filter if the solution is not clear. Acidify the solution strongly with HNO₃, and boil. If no precipitate separates, evaporate the liquid to dryness, moisten with HNO₃ (1.20), again evaporate to dryness, warm the residue with enough HNO₃ (1.10) to dissolve the salt present, and allow time for any precipitate to settle out. Whether a precipitate forms or not, add 2 c.c. H₂SO₄ (1.84), evaporate to the fuming-point, dilute with 5 c.c. HCl (1.02), and add a little granulated Zn. (Residue and solution, reject).

Notes.

1. The treatment with HF and H₂SO₄ serves to remove any SiO₂ that may have been introduced by the action of the alkaline solutions on the vessels or in the fusion with Na₂CO₃ and S. If not removed, it would separate with the H₂WO₄ when the aqueous solution of the fused mass is evaporated with HNO₃, and might obscure the test for tungsten.

2. When HNO₃ is added to an alkaline tungstate, H₂WO₄ separates as a white, flocculent precipitate, which upon boiling turns yellow, and becomes more compact. A very small quantity of tungsten, however, may not precipitate in this way; but it is separated as a heavy yellow powder, or as yellow flocks, or as a yellow stain on the sides of the dish, when the solution is repeatedly evaporated with acid.

3. In case a distinct yellow precipitate separates from the HNO₃ solution, the evaporation with H₂SO₄ and the addition of Zn, whereby a deep blue colouration and precipitate are produced if tungsten is present, serves only as an (almost superfluous) confirmation of the presence of that element. If, however, phosphate is present, and there is no yellow precipitate, the reduction test with Zn is essential, since H₂WO₄ does not separate from a solution containing a corresponding amount of this acid radical. Even a large quantity of phosphate does not, however, prevent the production of a strong blue colour with 1 m.grm. of tungsten.

Procedure 41.—If it is large enough in quantity, separate the H₂SO₄ precipitate (P. 39) from the filter, and transfer it to a porcelain crucible. If small in quantity, pour a portion of 2–3 c.c. (NH₄)₂S repeatedly through the filter till the precipitate is dissolved, collect the solution in a porcelain crucible, and evaporate it to dryness. Provide the crucible with a perforated porcelain cover through which passes a porcelain tube. Pass through the tube into

* From the *Technology Quarterly*, xvii., No. 3.

the crucible a slow current of H_2S gas, and heat the crucible (preferably within a cylindrical jacket with open ends, if the precipitate is large) first gently, then more strongly, and finally for five to thirty minutes, or until the whole mass becomes black, to the highest temperature attainable with a powerful burner. Allow the crucible to cool with the H_2S gas still passing through it. Rub its contents to a powder, and transfer them to a small Erlenmeyer flask. Pour into the crucible, if some of the substance is adhering to it, 2–3 c.c. HCl (1·20), warm, and pour the solution, together with 5–10 c.c. more HCl (1·20), into the flask. Cover the flask, and boil the liquid gently as long as the vapours continue to blacken filter-paper wet with a NaOH solution of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, replacing the acid which evaporates. Dilute the solution with its own volume of water, filter, and wash the residue. (Residue, P. 43; solution, P. 42).

Notes.

1. Precipitated WS_3 and V_2S_5 are sufficiently soluble in hot strong HCl to make their separation from SnS_2 and Sb_2S_3 by this solvent impracticable. By ignition in an atmosphere of H_2S , however, they are converted into WS_2 and VS_2 , which are entirely insoluble in boiling HCl (1·20). The ignition also serves to volatilise any As_2S_3 present, which otherwise would prevent the precipitation of H_2WO_4 in the subsequent test for tungsten. By the ignition SnS_2 and Sb_2S_3 are converted into black SnS and Sb_2S_3 respectively, which dissolves readily in HCl (1·20). If the ignition is not prolonged or intense enough, the hydrated SnS_2 is converted only into "mosaic gold" (SnS_2), consisting of golden yellow scales with metallic lustre; and this is only very slowly dissolved by the hot acid. The ignition must therefore be continued till the entire mass becomes black. Both MoS_3 and MoS_2 into which it is converted by ignition are entirely unattacked by boiling hydrochloric acid. The H_2S prevents the conversion of the sulphides into oxides, which occurs if air has access to them at a high temperature.

Procedure 42.—Evaporate the HCl solution (P. 28) to a volume of 2–3 c.c., and add an equal volume of water and about 0·5 gm. finely granulated Zn . Allow the action to continue for ten minutes. Decant the solution completely from the residue, allow any suspended particles to settle out from the liquid, and decant again. (Solution, reject). Add to the united residues 2–4 c.c. HCl (1·20), heat gently till the Zn has all dissolved, and then just to boiling unless the residue has previously disappeared, add half a volume of water, and pour the solution through a small filter into 5 c.c. nearly saturated HgCl_2 solution. (Residue, precipitate, and solution, reject).

Notes.

1. If tin seems to be present in considerable quantity (10 m.grms. or more), it may advantageously be tested for more simply by adding a portion of the HCl solution of the ignited sulphide, immediately after the H_2S is completely boiled out, to HgCl_2 solution; and in case a precipitate results, the treatment with Zn may be dispensed with; for after the ignition the tin is in the stannous state, and no other element can be present which reduces HgCl_2 , since ignited WS_2 , MoS_2 , and VS_2 are entirely insoluble in HCl , and since SbCl_3 does not cause reduction. In case, however, only a small quantity of tin (5 m.grms. or less) is present, it may become completely oxidised during the boiling of the HCl solution. In order that the tin test may be delicate, it is therefore necessary to follow the procedure and observe the precautions above indicated—especially to allow time for the complete reduction of the tin salt by the Zn , to secure solution of the tin by heating sufficiently with strong HCl , and to prevent oxidation of the stannous salt by carrying out rapidly the last steps in the process. By observing these precautions 1 m.grm. of tin is readily detected.

2. It is not necessary to test for antimony at this point, since it would have been precipitated in large part by H_2S in the first procedure of this group, and would pass, partly through that precipitation, and partly directly into the main HNO_3 solution.

Procedure 43.—Heat the residue insoluble in HCl (P. 41) in a covered vessel on a steam-bath with 2–8 c.c. HNO_3 (1·42) and 1–2 c.c. HCl (1·20) until it all dissolves, with the exception of a few black particles, or becomes pure yellow. If there is a residue, add an equal volume of water, allow the residue to settle, and decant the liquid through a filter. To the filtrate, or to the unfiltered solution if there was no residue, add 2–3 c.c. H_2SO_4 (1·84), evaporate till this acid fumes slightly, keep at that temperature for three or five minutes, cool, add 5 c.c. water, allow the residue to settle, and decant the solution through a filter. (Residues, P. 44; solution, P. 45).

Notes.

1. Even 100 m.grms. of ignited MoS_2 are completely dissolved by 10 c.c. of the mixture of HNO_3 and HCl ; and as a larger quantity cannot be present in this precipitate, there is no danger of its interfering with the tungsten test, provided the acid used is not evaporated off. If, however, the acid solution is allowed to concentrate, MoO_3 may separate as a white or light yellow powder, which will re-dissolve only in a very large quantity of HNO_3 . If this seems to have occurred, the residue should not be separated from the solution till after the evaporation with the H_2SO_4 . Black particles of carbon are usually left undissolved by the HNO_3 and HCl .

2. Even a small quantity (1–2 m.grms.) of tungsten, when present alone at this point, is readily detected by its separation as a yellow residue from the HNO_3 and HCl solution; but when much molybdenum (100 m.grms.) is also present, a considerable quantity of tungsten (at least 4 m.grms.) remains in solution. After the heating with the H_2SO_4 , however, a quantity even as small as 2 m.grms. always separates as a yellow compact powder.

3. If no yellow residue is obtained here or from the filtrate from the H_2SO_4 precipitate (P. 40) it does not show the absence of tungsten in the substance, since it may have passed entirely into the main HNO_3 solution (P. 6), as mentioned in P. 5, N. 1.

Procedure 44.—Add to the residues insoluble in HNO_3 and H_2SO_4 (P. 43) 2–3 c.c. HCl (1·12), evaporate to dryness, add 2 c.c. HCl (1·12) and a few granules of Zn .

Notes.

1. The evaporation with HCl removes the HNO_3 adhering to the residue. Even in the presence of 0·5 m.grm. W , a distinct blue colouration results, while with a somewhat larger quantity the mixture assumes a dark blue colour of great intensity. This colour is due to a suspended precipitate, which soon coagulates, consisting of a hydrated oxide intermediate between WO_3 and WO_2 . Molybdenum when present in strong HCl solution, such as is directed to be used in this test, does not give a blue colour with Zn , but there results a series of colours—yellow, dark orange, dark green, and, finally, dark olive-brown. In dilute HCl solution, however, molybdenum, even in moderate quantity, gives rise at once to a deep blue colouration of the solution.

Procedure 45.—Add to the H_2SO_4 solution (P. 43) of the ignited sulphides 1–2 c.c. 10 per cent KSCN solution and some granulated Zn .

Notes.

1. A red colouration which appears on the addition of the Zn shows the presence of molybdenum. Iron, if present as impurity, will give a red colour with the

KSCN alone, but this disappears almost immediately on the addition of the Zn. A negative result is of no significance, since molybdenum may have passed entirely into the main HNO_3 solution.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 5th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

(Concluded from p. 198).

76. "The Dynamic Isomerism of Phloroglucinol." By EDGAR PERCY HEDLEY.

It is well known that alkalis and acids affect the equilibrium existing between two isomerides in solution, and that the action of the alkali is to increase the oscillatory change in one direction, whilst the acid, on the other hand, decreases it.

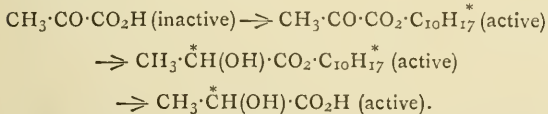
If phloroglucinol exists in solution in two forms—the enolic and ketonic modifications—then the position and persistency of the absorption band ought to undergo modification in the presence of alkali, and ought, in fact, to be displaced towards the less refrangible end of the spectrum. On the other hand, in the presence of acid, the persistency of the band ought to be decreased and become more like that of phloroglucinol trimethyl ether. These arguments were fully borne out by experimental test.

Lowry has pointed out that in some cases the solvent affects the equilibrium between dynamic isomerides. It was therefore thought advisable to examine whether in the case of phloroglucinol the solvent had any effect. Any non-ionising solvent would be suitable, provided it transmitted the ultra-violet light to a sufficient extent. Accordingly ether, a good and diastinic solvent, was used, and was found to have no effect on the spectrum.

The following conclusions were established:—(1) That in neutral solutions phloroglucinol exists in both modifications, the enol being greatly in preponderance over the keto-form; and (2) that this equilibrium is undisturbed by the class of solvent.

77. "Studies in Asymmetric Synthesis. V. Asymmetric Syntheses from *l*-Bornyl Pyruvate." By ALEXANDER MCKENZIE and HENRY PERR.

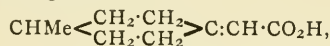
The authors have examined the reduction of *l*-bornyl pyruvate by aluminium amalgam, and find that an asymmetric synthesis of *l*-lactic acid may be accomplished in accordance with the scheme:—



The actions of magnesium ethyl iodide, magnesium isobutyl iodide, magnesium phenyl bromide, and magnesium α -naphthyl bromide respectively on *l*-bornyl pyruvate, and of magnesium isobutyl iodide and magnesium α -naphthyl bromide respectively on *l*-menthyl pyruvate, have been studied. The results obtained are contrasted with those recorded in a previous paper with the object of comparing the effect, first, of the active menthyl and bornyl groups, and, secondly, of the various alkyl (or aryl) halides used on the extent of the asymmetric syntheses of the resulting substituted glycolic acids.

78. "1-Methylcyclohexylidene-(4)-acetic Acid." By WILLIAM HENRY PERKIN, jun., and WILLIAM JACKSON POPE.

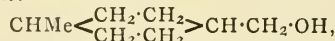
The current number of the *Berichte* (1906, xxxix., 1171) contains a paper by W. Marckwald and R. Meth, in which these investigators describe the synthesis of an acid to which they assign the formula—



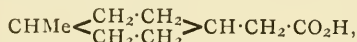
and which they have resolved into active modifications by fractional crystallisation of the cinchonine salts.

During the last three years, the authors have been engaged in an attempt to prepare a substance which, while not containing an asymmetric carbon atom is yet capable of existing in optically active modifications, and it is noteworthy that one of the substances selected for examination was methylcyclohexylideneacetic acid. Since, however, the method of preparation is quite different from that of Marckwald and Meth, and the results obtained are not in agreement with theirs, the following preliminary account of the authors' experiments is now put forward.

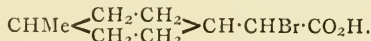
Ethyl hexahydro- β -toluate is converted into hexahydro- β -tolylcarbinol—



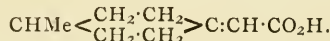
by reduction with sodium and alcohol. This carbinol distils at 197° , and is readily converted into hexahydro- β -tolyl bromide (b. p. $135^\circ/150$ m.m.) by the action of hydrobromic acid at 120° . When this bromide is heated with potassium cyanide and the product hydrolysed, it yields hexahydro- β -tolylacetic acid,—



which melts at 73 – 74° , and is readily acted on by phosphorus pentachloride and bromine with formation of α -bromohexahydro- β -tolylacetic acid (m. p. 78°),—

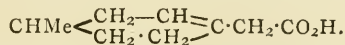


The ester of this bromo-acid is decomposed by boiling with diethylaniline with elimination of hydrogen bromide and formation of ethyl methylcyclohexylideneacetate, which distils at $158^\circ/100$ m.m., and, on hydrolysis, yields the free acid,—

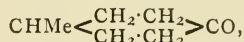


The methylcyclohexylideneacetic acid thus obtained crystallises from formic acid in glistening plates, and melts at 70 – 71° , whereas the acid described by Marckwald and Meth, and to which these authors assign this constitution, melts sharply at 40 – 41° .

The method of preparation seems to leave no doubt that the acid melting at 70 – 71° is methylcyclohexylideneacetic acid, whilst the acid of melting-point 40 – 41° described by Marckwald and Meth is possibly the isomeric acid,—



The fact that, when heated with strong caustic potash, it is decomposed into 4-methylcyclohexanone,—



and acetic acid is easily explained on this assumption.

It is well known that an unsaturated acid which contains the double linking in the $\beta\gamma$ -position is readily converted, by the action of strong caustic potash, into the corresponding $\alpha\beta$ -unsaturated acid, and this isomeric change may have taken place in the case of Marckwald and Meth's acid prior to the decomposition into methylcyclohexanone and acetic acid.

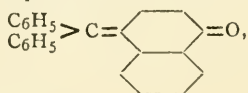
The authors are investigating this matter further, and are also engaged in a series of experiments with the object of resolving the acid melting at 70 – 71° into optically active modifications.

79. "Condensation of Benzophenone Chloride with α - and β -Naphthols." By GEORGE WILLIAM CLOUGH.

By heating α -naphthol with benzophenone chloride, the author has prepared di- α -hydroxynaphthylidiphenylmethane, the acetyl and benzoyl derivatives of which have also been obtained.

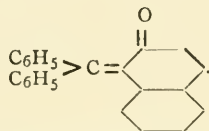
When benzophenone chloride was added to a boiling solution of β -naphthol in xylene, the product obtained was di- β -naphthoxydiphenylmethane, which is hydrolysed by dilute sulphuric acid into β -naphthol and benzophenone.

The action of sodium α -naphthoxide on benzophenone chloride resulted in the formation of the inner anhydride of α -naphthylidiphenylcarbinol, and the same substance was also obtained by adding α -naphthol to a boiling solution of the ketone chloride in light petroleum. This compound is yellow, and the quinonoid formula,—



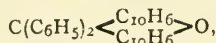
has been assigned to it.

Sodium β -naphthoxide interacts with benzophenone chloride in a similar manner to form a red, crystalline substance, to which the following formula is ascribed:—



These coloured compounds are soluble in concentrated sulphuric, nitric, and hydrochloric acids respectively, the α -compound giving violet and the β -compound green solutions in these acids.

A condensation of benzophenone itself with α -naphthol has also been effected by heating these substances in the presence of zinc chloride and hydrogen chloride at 150–160°. The product obtained was α -oxydinaphthylidiphenylmethane,



the condensation resembling that of acetone with α -naphthol (Dianin, Abstr., 1893, i., 214). Its solution in concentrated acid is yellow and exhibits a green fluorescence.

80. "The Constitution of Cærulignone (Cediret)." (A Preliminary Note). By JAMES MOIR.

On the authority of Liebermann, Hofmann, and others, it has been accepted that cærulignone is tetramethoxydiphenoquinone; in addition, several strictly analogous substances have been prepared and formulated by their discoverers as the corresponding tetra-chloro-, -bromo-, -amino-, and -hydroxy-derivatives of diphenoquinone.

Now diphenoquinone itself,—



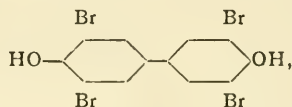
has recently been prepared by Willstätter and Kalb (Ber., 1905, xxxviii., 1232), and the author finds that its properties are quite different from those of cediret and its analogues, and that, in fact, diphenoquinone is a true para-quinone, whereas cediret and its analogues do not possess any quinonoid property except colour. Their properties are:—(1) Complete insolubility in organic solvents; (2) metallic lustre; (3) decomposition on heating without melting or subliming; (4) intense colourations—blue to crimson—with sulphuric acid; (5) characteristic colour reactions with alkali; (6) production of complex sulphates of high molecular weight through the action of sodium sulphite. Such properties as these indicate molecular complexity and a polyquinonoid constitution.

The author finds that the "diphenoquinhydrone" of Willstätter and Kalb (*loc. cit.*) is the true parent substance of cediret, since it possesses all the foregoing properties. Nevertheless, it is doubtful at present whether this sub-

stance is really a simple quinhydrone; that is, a direct additive product of diphenoquinone and diphenol; some of its reactions indicate a larger molecular weight and higher percentage of oxygen than the formula $\text{C}_{24}\text{H}_{18}\text{O}_4$ requires.

The substance described by Magatti as tetrabromodiphenoquinone (Ber., 1881, xiii., 226) has been studied more in detail. In the first place, it is quite different from the true tetrabromodiphenoquinone, which the author has prepared by oxidising tetrabromodiphenol with lead peroxide, and which forms transparent orange crystals, is soluble in many organic solvents, and otherwise resembles diphenoquinone. Magatti's substance contains a lower percentage of bromine than is required by such a formula as $\text{C}_{12}\text{H}_4\text{O}_2\text{Br}_4$, and Magatti's analysis in support of this formula may be set aside as probably fictitious, since he has miscalculated the theoretical proportion of bromine and yet his analysis agrees with the assumed theoretical value. The compound gives, even in traces, a magnificent crimson shade with sulphuric acid, and on digestion with alkali forms a derivative which closely resembles indigotine in colour and coppery lustre; this can be also prepared directly by careful oxidation of an alkaline solution of tetrabromodiphenol with iodine or potassium ferricyanide.

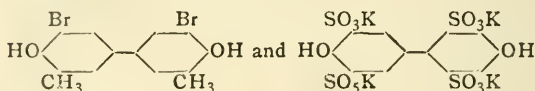
The orientation of the bromine atoms in tetrabromodiphenol has been settled to be as in the formula—



(3 : 5 : 3' : 5'-tetrabromo-4 : 4'-diphenol).

since the sole product of the oxidation of its diacetate was 3 : 5-dibromo-4-acetylbenzoic acid.

Finally, two new analogues of cediret have been prepared by oxidising the compounds—



respectively; the former has a green, graphite-like lustre, and gives a maroon shade with sulphuric acid, whilst the latter, easily soluble in water, has a very dark indigo colour.

81. "A Comparative Crystallographic Study of the Perchlorates and Permanganates of the Alkalis and the Ammonium Radicle." By THOMAS VIPON BARKER.

The perchlorates of potassium, rubidium, caesium, and ammonium form an isomorphous group similar to that of the permanganates of the same metals, which were investigated by Muthmann. The salts are orthorhombic, and possess perfect cleavages parallel to the basal plane and the prism. All the constants of rubidium perchlorate determined are intermediate between those of potassium and caesium perchlorates; ammonium perchlorate, again, lies very close to rubidium perchlorate, as does also thallium perchlorate according to Roscoe's measurements. The series, therefore, resembles the isomorphous groups investigated by Tutton. On comparing the perchlorates with the permanganates, it is found that the effect of replacing an atom of chlorine by one of manganese is much the same as that induced by the substitution of sulphur by selenium, say, in the sulphates of the same metals. The crystallographic evidence for placing manganese in the seventh group of the periodic classification, so far as such evidence goes, is therefore of the strongest possible kind.

Five crops of isomorphous mixtures of potassium perchlorate and permanganate of varying composition were measured. In one crop only, corresponding very closely to the formula $\text{K}_2(\text{ClO}_4)(\text{MnO}_4)$, were abnormal angles found; that is, angles the values of which lie outside those of the constituent salts; moreover, these angles were all in one zone, in which the faces were possibly vicinal,

82. "Contributions to the Theory of Isomorphism based on Experiments on the Regular Growths of Crystals of one Substance upon those of Another." By THOMAS VIPOND BARKER.

The parallel growths of sodium nitrate on cleavage surfaces of calcite are independent of the locality or variety of the calcite so long as a good fresh cleavage surface is obtainable. Regular growths of rhombohedra of the nitrate were also obtained upon certain other forms of calcite, for example, the prism, scalenohedron, a steep rhombohedron, and the rare prism $\{\bar{1}10\}$; in all cases a pair of similar edges of the calcite and sodium nitrate are congruent. The effect of a magnetic field on the orientation of the crystals was purely negative. No parallel or regular growths could be obtained on the other minerals of the calcite group—dolomite, calamine, chalybite, rhodocrosite, diallogite, and breunnerite—nor on barytocalcite. The failure of the latter minerals to induce a parallel deposition is probably not due to a difference of symmetry or of angle (or axial ratio), but to a dissimilarity of molecular volume, and hence of topic axes also.

This view is strengthened by the discovery of parallel growths among the members of another and more numerous series of isostructural minerals and salts; potassium perchlorate and permanganate are deposited (from aqueous solution) upon barytes, celestine, and anglesite in parallel position, whereas the perchlorates of rubidium, caesium, ammonium, and thallium and the permanganates of rubidium, caesium, and ammonium are not. Here, again, those salts which do form parallel growths are characterised by a closeness of molecular volume to those of the minerals on which they are deposited, while similarity of angle (or of axial ratios) is not sufficient to induce a parallel growth. If the above substances be arranged in order of topic axes, it is seen that potassium perchlorate and permanganate fall next to the three minerals mentioned.

Since calcite and sodium nitrate resemble each other so closely in all their physical properties, and since calcite relieves supersaturation in a metastable solution of the nitrate, the conclusion is drawn that these isostructural substances are also to be regarded as isomorphous, although mixed crystals are not obtainable.

Many unsuccessful attempts were made to obtain regular growths of other salts on other minerals, more especially of cubic salts on cubic minerals and potassium nitrate on aragonite; but regular growths of potassium bromide, iodide, and nitrate and sodium nitrate on mica, and of quinol on calcite, were obtained.

All the perchlorates and permanganates mentioned yield parallel growths on each other, but it was found that pairs of isomorphous salts, the molecular volumes of which are almost identical, form zonal growths ("Schichtkrystalle") rather than parallel growths.

83. "Constitution of Silicin. Synthesis of Pentamethyl Salicin." By JAMES COLQUHOUN IRVINE and ROBERT EVSTAFIEFF ROSE.

Salicin was alkylated by means of the joint action of silver oxide and methyl iodide, with the production of pentamethyl salicin. The process was carried out in the first instance in methyl-alcoholic solution, and, after the alkylation had proceeded far enough, methyl iodide was used as solvent. The product crystallised in delicate needles (m. p. 62–64°), readily soluble in organic solvents and giving $[\alpha]_D^{20} = 52.15^\circ$ in alcoholic solution.

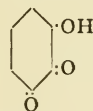
Emulsion was found to be without action on the compound, and even dilute mineral acids readily converted it into a resinous mass resembling saliretin. The hydrolysis was therefore carried out indirectly by prolonged heating at 100° of a solution of the substance in methyl alcohol containing 0.25 per cent of hydrochloric acid. Tetramethyl glucose was thus produced, and afterwards converted into the equilibrium mixture of α - and β -tetramethyl methylglucosides. The alkylated glucosides were isolated and then hydrolysed to give tetramethyl glucose (m. p. 84–86°).

This reaction proves that salicin (and hence also helicin and populin) contains the same γ -oxidic linking as the methylglucosides and sucrose.

Further evidence on this point was obtained in the synthetical preparation of pentamethyl salicin. On heating saligenin and tetramethyl glucose to 120° in benzene containing 0.25 per cent of hydrochloric acid, condensation took place with the formation of a mixture of saligenin tetramethyl glucosides and octamethyl glucosidoglucoside. After separation of the alkylated disaccharide, the mixture was methylated by the silver oxide reaction and a compound, identical in every respect with the pentamethyl salicin prepared directly from the glucoside, was isolated from the product.

84. "A Product of the Action of Isoamyl Nitrite on Pyrogallol." By ARTHUR GEORGE PERKIN and ALEC BOWRING STEVEN.

When an alcoholic solution of pyrogallol is oxidised with acetic acid and isoamyl nitrite, a small quantity (1.3 per cent) of pale salmon-coloured leaflets separate (m. p. 203°). The main bulk of this product is colourless, may be obtained as minute prisms melting at 206–208° with effervescence, and has the composition $C_6H_4O_3$. With acetic acid and zinc dust it gives pyrogallol with acetic anhydride and zinc dust triacetylpyrogallol (m. p. 160–162°); its acetyl derivative, $C_6H_3O_3(C_2H_3O)$, forms colourless leaflets (m. p. 283–285°), and also yields triacetylpyrogallol in a similar manner. The substance $C_6H_4O_3$ dissolves sparingly in boiling acetic acid and alcohol with some decomposition, and by means of boiling water yields purpurigallin, $C_{11}H_8O_5$. The reaction studied in detail with the crude substance (m. p. 203°) showed that in this way a compound $C_{12}H_{10}O_7$? (colourless prisms, m. p. 242–243°) and an orange-brown resin, both readily soluble in water, are also formed. Owing to the poor yield it has not been possible to study this product further, but it appears likely that it may consist of hydroxy-*o*-benzoquinone:—



85. "A Reaction of Ellagic and Flavellagic Acids." By ARTHUR GEORGE PERKIN.

When ellagic acid is heated at about 230° with 100 per cent sulphuric acid, it is oxidised with formation of a new compound which crystallises from pyridine in small, yellow, prismatic needles and is soluble in strong alkalis with a greenish yellow tint, changing to blue on dilution. It appears to have the formula $C_{14}H_6O_{10}$ (found, $C = 50.01$; $H = 2.17$), gives a hexacetyl derivative [needles, $C_{14}H_{10}(C_2H_3O)_6$, m. p. 324–329°; found, $C = 53.18$; $H = 3.32$; $C_{14}H_6O_{10} = 57.24$], and dyes mordanted fabrics more readily than ellagic acid. Flavellagic acid behaves similarly [found for $C_{14}H_6O_{10}$, $C = 50.09$; 2.08 ; and for $C_{14}O_{10}(C_2H_3O)_6$, $C = 53.12$; $H = 3.34$ per cent].

86. "Some Thio- and Dithio-carbanide Derivatives of Ethylenaniline and the Ethylenetoluidines." By OLIVER CHARLES MINTY DAVIS.

In the interaction of ethylenaniline and the ethylenetoluidines with the thiocarbimides, several instances of steric hindrance were observed, the position of the substituent methyl group in the ethylenetoluidines and the tolylthiocarbimide having an important bearing both on the time of reaction and also on the nature of the product.

One molecule of ethylenaniline unites with two molecules of allyl-, phenyl-, *o*-tolyl-, or *p*-tolyl-thiocarbimide to form symmetrical dithiocarbamide derivatives, but with *m*-tolylthiocarbimide only one molecule of each unites to form an asymmetrical substituted thiocarbamide. Ethylene-*o*-toluidine reacts with difficulty to give asymmetrical derivatives with phenyl-, *m*-tolyl-, and *p*-tolyl-thiocarbimides, whilst with allyl- and *o*-tolyl-thiocarbimides the

yield was exceedingly small. Ethylene-*m*-toluidine gives symmetrical derivatives with phenyl- and *p*-tolyl-thiocarbimides, but with allyl-, *o*-tolyl-, and *m*-tolyl-thiocarbimides asymmetrical derivatives result. Ethylene-*p*-toluidine gives an asymmetrical derivative with *m*-tolylthiocarbimide, but with other thiocarbimides symmetrical derivatives are formed.

With the ethylenetoluidines, the ortho- and meta-positions therefore seem to modify the reactions, but with the thiocarbimides the meta-position only has this effect.

The foregoing compounds interact with mercuric oxide in alcoholic solution when heated at about 140° in sealed tubes, oxygen replacing sulphur. The product from ethylenedianiline and phenylthiocarbimide appears to be identical with a compound synthesised from ethylenedianiline and phenylcarbimide.

OBITUARY.

PROF. PIERRE CURIE.

ONE of the saddest deaths it has been our painful duty to record is that of the late Prof. Pierre Curie, who, with his wife, was the discoverer of the element radium. He met his death by being knocked down by a waggon while crossing the Rue Dauphine, Paris, on April 19th; his head was crushed, and death must have been instantaneous.

By his death, which has occurred in the flower of his manhood, we lose a great personal friend, and the world loses one of its most brilliant scientific men. We well remember our first visit to his laboratory some years ago, when much less was known of radium than is now. It was as modest and unassuming in appearance as was the great discoverer himself; it was, in fact, little better than a shed almost hidden by the surrounding buildings; but in this shed was first brought to light an element which, though even now known to exist in only the most minute proportions in any known mineral, has already revolutionised the whole train of scientific thought with regard to the construction of the atom and the conservation of matter as we know it. It is needless in these pages to do more than thus lightly pass over the properties of radium—they are so well known to all our readers. We have here to do more with the man himself than the details of his work.

Prof. Curie was born in Paris in the year 1859, and was therefore forty-six years of age; he obtained practically all his education in free classes under his father's guidance and as assistant in chemical laboratories, and finally graduated at the Sorbonne, where he attained the degree of Doctor of Science. His first researches were on the subject of piezo-electricity, in conjunction with his brother, and the skill and experience he attained in this work in the construction and manipulation of electrometers, guard-ring condensers, aperiodic balances, &c., must have been of the greatest service to him in his later more important work carried out in conjunction with his wife.

In 1895 Prof. Curie married Marie Skłodowska, one of the senior students at the Municipal School at which he was Professor, and it was through the combined efforts of these two highly-gifted students of Nature that the wonderful results were obtained that so startled the scientific and popular world a few years ago.

In 1903 M. and Mme. Curie received the Davy Medal of the Royal Society, and they shared with M. Branly the Osiris Prize and with M. Becquerel the Nobel Prize for physics.

Like many other great discoveries, theirs was received at first with indifference—even so recently as in the 1900 Exhibition in Paris, where it was practically overlooked; then with scepticism, until Mme. Curie published her

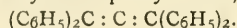
famous Thesis which gained for her the degree of Doctor of Physical Science. After this time honours and prizes were showered upon them, and the name of Curie obtained an imperishable place on the scroll of fame.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

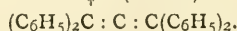
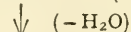
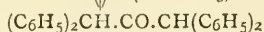
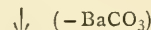
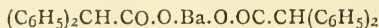
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 5, 1906.

New Aromatic Hydrocarbons.—D. Vorländer and C. Siebert.—By distilling barium diphenyl acetate a new crystalline colourless hydrocarbon is obtained; this the authors find to be sym-tetraphenyl allene,—



Apparently a part of the salt yields tetraphenyl acetone, and this is decomposed to form tetraphenyl allene and water on distillation.

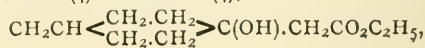


The water converts another part of the barium diphenyl acetate into diphenyl methane. The new substance is unsaturated, melts at 164°, and gives very unstable addition products with sulphuric acid and halogen hydrides. When treated with hydriodic acid and phosphorus or sodium and alcohol, it takes up hydrogen and yields a saturated hydrocarbon tetraphenyl propane, $(C_6H_5)_2CH.CH_2.CH(C_6H_5)_2$ (m. p. 140°). When oxidised with chromic acid it yields benzophenone and carbon dioxide. It is very readily attacked by acids and an isomeric hydrocarbon (m. p. 135°) is formed when it is heated with acetic acid or aqueous hydrochloric acid, or when it is allowed to stand with concentrated sulphuric acid or halogen hydrides in glacial acetic acid. This isomeric substance is also unsaturated, but yields no benzophenone with chromic acid.

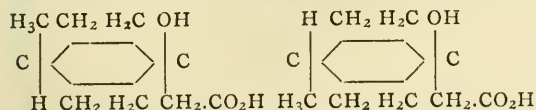
Combustion of Cadmium.—W. Manchot.—It is generally assumed that the brown fumes which are formed when cadmium is burnt consist of cadmium oxide, but it may very easily be shown that they contain cadmium peroxide also. If the fused metal is ignited and the fumes are collected in a beaker, and acidified potassium iodide added, a blue coloration appears. It is essential that the combustion should take place at as low a temperature as possible; if the metal is coated with a layer of oxide the experiment fails because it has to be heated too strongly in order to produce the fumes. In this case it may be observed that a potassium iodide solution, which has already turned blue, is again decolorised, as metal distils with the oxide. In this respect cadmium is allied to the alkali metals and magnesium.

Optically Active Compounds which contain no Asymmetric Atom.—W. Marckwald and R. Meth.—Inositol has hitherto been the only compound known which is optically active and yet contains no asymmetric atom, but the authors have now succeeded in preparing another similar compound. Starting from 1-methyl-cyclohexanone—

(4), $CH_3.CH < \begin{smallmatrix} CH_2.CH_2 \\ CH_2.CH_2 \end{smallmatrix} > CO$, by the action of brom- or iodo-acetic ester and magnesium, they obtained 1-methyl-cyclohexanol-(4)-acetic ester-(4),—



from which a mixture of two crystalline acids could be obtained. These two acids have the formulæ:—



If the cinchonine salts of these acids are prepared in alcoholic solution a syrup is obtained which crystallises after it has stood for some time in the desiccator. When the crystals are washed with ligroin and the salt decomposed with sulphuric acid the *d*-acid is obtained, while the ligroin solution with which the cinchonine salt was washed contains the *l*-acid.

MEETINGS FOR THE WEEK.

- MONDAY, 7th**—Society of Arts, 8. (Cantor Lectures). "Ivory in Commerce and in the Arts," by Alfred Maskell.
Royal Institution, 5. General Monthly Meeting.
Society of Chemical Industry, 8. "Notes on the Gutzeit Test for Arsenic," by J. Goode and P. M. Perkin. "Separation of Brucine and Strychnine—Influence of Nitrous Acid in Oxidation by Nitric Acid," by W. C. Reynolds and R. Sutcliffe. "Absorption of Gallic Acid by Organic Colloids," by W. P. Dreaper and A. Wilson.
- TUESDAY, 8th**—Royal Institution, 5. "Glands and their Products," by Prof. William Stirling, M.D., &c.
Society of Arts, 8. "Damascening, and the Inlaying and Ornamenting of Metallic Surfaces," by Sherard Cowper-Coles.
- WEDNESDAY, 9th**—Society of Arts, 8. "Bridge Building by means of Caissons, including remarks upon Compressed Air Illness," by Prof. Thomas Oliver, M.D., &c.
- THURSDAY, 10th**—Royal Institution, 5. "The Expansion of Old Greek Literature by Recent Discoveries," by the Rev. J. P. Mahaffy, C.V.O., D.D., &c.
- FRIDAY, 11th**—Royal Institution, 9. "Some Astronomical Consequences of the Pressure of Light," by Prof. J. H. Poynting, F.R.S., &c.
Physical, 8. "Effect of Rapid Discharge on the Throw of a Galvanometer," by A. Russell. Exhibition of Lippmann Capillary Dynamo and Electromotor, by Prof. H. A. Wilson. Exhibition of an Apparatus for Demonstrating the Movements of the Diaphragms of Telephonic Transmitters and Receivers and the Current flowing into and out of the Cable during Speech, by W. Duddell.
- SATURDAY, 12th**—Royal Institution, 3. "English Furniture in the Eighteenth Century," by Prof. Charles Waldstein, Ph.D., &c.

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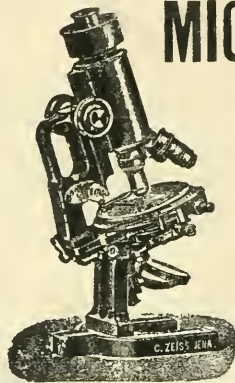
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ON

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REPRINTED from the CHEMICAL NEWS.

CONTENTS.

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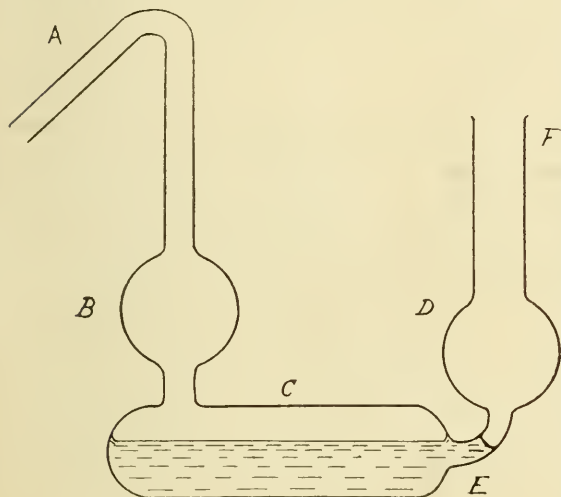
THE CHEMICAL NEWS.

VOL. XCIII., No. 2424.

A NEW FORM OF ABSORPTION-TUBE.

By EDGAR PHILIP PERMAN.

IN estimating chlorine (from peroxides, &c.), ammonia, and other substances in which an absorption-tube is used, difficulty is often experienced owing to the condensation of steam or the too rapid absorption of the gas evolved. The result is that some of the absorbing liquid is carried back into the flask in which the gas is generated. This difficulty can be entirely overcome by the use of a tube



of the pattern shown in the accompanying diagram. Convenient dimensions are C, 1 inch diameter, 3.5 inches long, B and D 1.25 inches diameter. The liquid should just close the narrow tube at E. A is connected with the generating flask by rubber, cork, or ground-glass joint, and a guard tube, containing glass beads moistened with the absorbent, may be connected to F. I have tested the tube as severely as possible, but it has never failed.

University College, Cardiff.

DETERMINATION OF SULPHUR IN PYRITES.

By C. R. GYZANDER,
Chemist to the Cochrane Chemical Co., Boston, U.S.A.

THOUGH there exists no method for determining what might reasonably be termed available sulphur in pyrites, from the sulphuric acid manufacturers point of view, Dr. Lunge's method aims at least towards this end; hence the reason for its almost universal adoption for the valuation of pyrites for the sulphuric acid trade.

But this method requires a good deal of manipulative skill, strict attention to details, is not well adapted for carrying on many simultaneous determinations, and is rather tedious. It is therefore much more suitable for the student than for the works chemist.

Of the many proposed improvements of this method none has yet proved of any particular value, either as regards final results or time required. But although the

time required for an analysis of this nature is secondary in importance, a method which materially shortens it without sacrificing accuracy is certainly to be preferred.

Years ago an improvement of the Lunge method was proposed, based on the reduction of the iron to the ferrous state by means of thiosulphate before precipitating with barium chloride.

Obviously the results, as regards percentage of sulphur, must be very incorrect by this method, but nevertheless it taught one important and valuable lesson, namely, that it was possible to precipitate BaSO_4 in the presence of iron, and free from iron when the latter is in the ferrous condition. With a suitable reducing agent, therefore, a step in the direction of shortening the time had been found. Hydroxylamine hydrochlorate proved to be an ideal reducing agent, and comparative tests showed that the results obtained were the same as with the Lunge method; hence no sacrifice of accuracy.

As regards the amount of ore needed for a sulphur determination, this will largely depend upon the sensitivity of the balance used, and it may therefore be necessary for some to use as much as 1 gram. of ore, as has also been proposed. With a sensitive balance there is no need of using over 0.5 gram., as Dr. Lunge recommends, and even 0.2 gram. is sufficient for all practical purposes.

I work as follows:—

Two-tenths of a gram. of ore ground until almost free from grit in an agate mortar is treated with a mixture of 5 c.c. concentrated HCl and 15 c.c. concentrated HNO_3 in a small covered beaker, as recommended by Dr. Lunge.

This acid mixture is far preferable to bromine or fuming nitric acid, and has never yet failed to oxidise the whole of the sulphur for this amount of ore. With 0.5 or 1 gram. of ore it not unfrequently fails in this respect, as do also the other two reagents mentioned.

The beaker is placed on the water-bath, and when all action has ceased the cover is rinsed off with distilled water, removed, and the contents of the beaker evaporated to dryness. When dry, moisten with a little water, add 5 c.c. concentrated HCl , and again evaporate to dryness. When dry the second time add 100 c.c. distilled water, 1 c.c. concentrated HCl , and 3 c.c. hydroxylamine hydrochlorate solution containing 1 oz. of the salt in 500 c.c. distilled water. When the iron is reduced—that is, when the solution is colourless—filter and wash with hot water exactly as recommended by Dr. Lunge. Heat the filtrate to near boiling, and add 10 c.c. of a 10 per cent BaCl_2 solution. Place beaker on water-bath to settle, then remove to the bench to cool to room temperature before filtering off the BaSO_4 , which, after being washed free from chlorides, is dried, incinerated, and weighed as usual.

It is immaterial, as far as the amount of sulphur precipitated is concerned, whether one uses hot BaCl_2 as recommended by Dr. Lunge, or drops the cold BaCl_2 solution, but the manner of adding the BaCl_2 solution may greatly affect the filterability of the BaSO_4 formed. With the Lunge method one has very little trouble in producing a coarse, easily settling precipitate, due, presumably to the action of the large amount of ammonium salts present, but this precipitate is rather difficult to wash free from chlorides.

With the hydroxylamine method the BaSO_4 is in a much finer state of division, but with proper care it is dense enough for any ordinary filter-paper not too thin. I succeed best when dropping in the cold BaCl_2 solution slowly and with stirring to the almost, but not quite, boiling solution, the whole operation occupying about two minutes. One may transfer the BaSO_4 precipitate to the filter at once without previous decantation with hot water, as it washes very much more readily than does that obtained by the Lunge method. One may carry on any number of simultaneous determinations without fear that any inattention to a funnel at a particular time will cause complications, as may be the case with the Lunge method if one has too many ferric hydrate separations at one time, or if, being called away to attend to some other work for a

little while, the precipitate of ferric hydrate becomes too dry and assumes a lumpy instead of a flocculent appearance on further treatment with water, and which leads to a considerable retention of sulphur, even though by proper care in precipitation with ammonia one has guarded against the formation of baric salts.

The following results were obtained by myself with the hydroxylamine method, and by a New York chemist by the Lunge method.

	Hydroxylamine method.	Lunge's method.
Canadian ore (1) ..	42'40	42'29
" " (2) ..	44'20	44'14
Spanish " ..	46'16	44'19

It will therefore be seen that the two methods give the same result, while that with hydroxylamine is much shorter and more convenient.

THE CHEMICAL ELEMENTS.

A NEW CLASSIFICATION.

By GEO. WOODIWISS.

THE accompanying diagram is designed with the object of illustrating the inter-relationship of the chemical elements as shown by their relative weights. The weights of the elements may be considered from two extremes of temperature; between these two extremes the ratio of weights may be altered by alteration in temperature, but the limit of alteration is arrived at at these extremes. The weight of the elements may be represented in the first extreme by the specific gravity in the atomic state, and in the second extreme in the solid state by the specific gravity at the absolute zero of temperature. And for the purpose of the diagram the latter may be represented by the specific gravity of the elements as compared at 0° C., the figures in brackets indicating comparison in the liquid state.

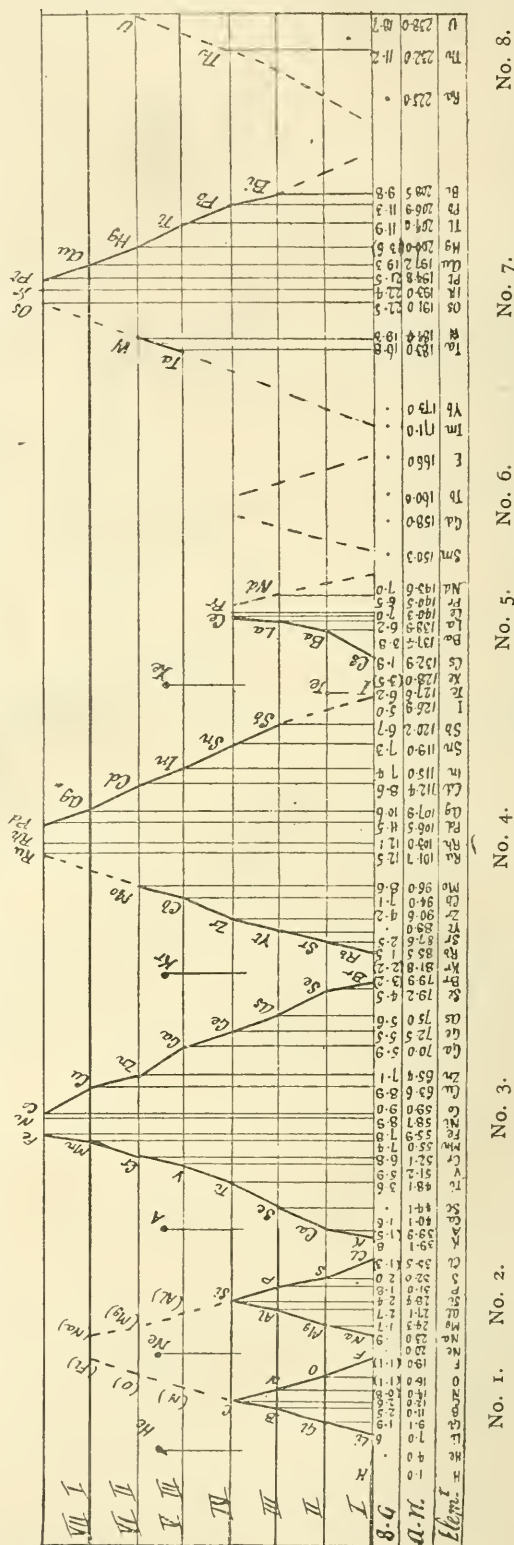
If we form a list of the elements in the order of their atomic weight, by an examination of this alone we find little indication of a periodicity, but if we combine with this a knowledge of the properties of the elements, we are then in a position to prove a periodicity. This has been conclusively shown by Mendeleeff.

If we form a list of the elements in the order of their atomic weight and divide this list into periods as indicated by the specific gravity in the solid state, the analogous elements are shown in an order differing from that of Mendeleeff, but in a clear and remarkable manner.

In the diagram, therefore, the elements are shown horizontally to scale according to their atomic weight, and vertically on eight equidistant lines of valency according to their specific gravity. The diagram is thus divided into a series of eight colonies or tents of the elements; these tents have a most remarkable relationship to each other, and particularly so when taken in evident pairs. Many of the characteristics of the elements are repeated in a more or less degree by those occupying analogous positions. Those noted for their power of occluding gases, for instance, are found at the crown of the tents; copper and silver, the free conductors of heat and electricity, occupy analogous positions, as do the alkali metals, the alkaline earths, and many others. Those elements occupying corresponding positions on opposite sides of the tents have more or less opposite properties, as potassium and bromine, manganese and copper, &c. The elements on the left slope of the tents have increased specific gravity with increase of atomic weight; those on the opposite side have a decrease of specific gravity with the increase of atomic weight. The heavy metals are separated from the light metals, and the non-metals are separated from them both, and each in their respective tent gradually merge the one into the other.

That the specific gravity is a guide as to the formation of these tents may be illustrated by tents No. 1 and No. 2, for by ignoring specific gravity these two may be combined

A DIAGRAM OF ATOMIC WEIGHT AND SPECIFIC GRAVITY OF THE CHEMICAL ELEMENTS.



to form one, as shown by the dotted lines in the diagram, the altered position of the elements being shown in brackets. The tent so formed is in many respects similar to the larger tents; nevertheless, it is still evident that it is quite distinct, is insufficient in width, and could never form one similar to the larger kind. It serves to show, however, that there is a connection between the upper and lower parts of the larger tents; for if we now invert the right-hand side of all the tents (from the base to the seventh line) the elements are then on oblique lines, almost but not quite parallel, and the elements are then in the order of the periodic system of Mendeleeff; thereby it may be shown that in the larger tents the elements in the upper part on the one side are in many ways connected with those in the lower part of the opposite side when taken in the inverse order.

The position of hydrogen is not indicated in the tents, neither are the gases helium, neon, argon, krypton, and xenon; these inert gases are shown according to their atomic weight, and, with the exception of argon, find a position between the tents, and as they are not known to have chemical affinity they are not shown on any line of valency.

THIRTEENTH ANNUAL REPORT
OF THE COMMITTEE ON ATOMIC WEIGHTS.
DETERMINATIONS PUBLISHED IN 1905.*

By F. W. CLARKE.

(Concluded from p. 205).

Metals of the Rare Earths.

A CONSIDERABLE number of memoirs upon the rare earths have appeared in the course of the year, with incidental data on the subject of their atomic weights. In only two of them was the determination of atomic weight the principal feature, the paper by Urbain (*Comptes Rendus*, xl., 583) on gadolinium being the most important. Urbain prepared his material by many fractionations of gadolinium-nickel nitrate, and analysed a number of distinct preparations of the octohydrated gadolinium sulphate. According to Eberhard (*Zeit. Anorg. Chem.*, xlv., 375), who has studied several rare earths spectroscopically, Urbain's material for samarium, gadolinium, and europium was exceedingly good, if not absolutely free from admixtures. Bettendorff's samarium preparation contained other earths.

I	Li	Na	K	Rb	Cs	—	—	—	Cu	Ag	Au	—	I
	Fl	Cl	Br	I	—	—	—	—	Mn	—	—	—	VII
II	Gf	Mg	Ca	Sr	Ba	—	—	—	Zn	Cd	Hg	—	II
	O	S	Se	Te	—	—	—	—	Cr	Mo	W	U	VI
III	B	Al	Sc	Yt	La	—	—	—	Ga	In	Tl	—	III
	N	P	As	Sb	Nd	—	Bi	—	V	Nb	Ta	—	V
IV			Ti	Zr	Ce	—	—	Th	Fe	Ru	Os	—	
	C	Si			Pr	—			Ni	Rh	Ir	—	IV
			Ge	Sn	—	—	Pb	—	Co	Pd	Pt	—	

An item of interest is the systematic arrangement of the non-metallic elements. The first four tents contain five, four, three, and two of these elements respectively, in each case the more active element being found at the base and on the right-hand side of the tent; this symmetrical arrangement and gradual decrease suggesting a further decrease in the remaining tents.

By taking consecutively from tent to tent, the elements from analogous positions, the accompanying table is formed.

It is of interest to note the lowering of the melting-point from lithium to caesium, and the rise in the melting-point from fluorine to iodine, the one being in the reverse order to the other.

It will be noticed there is no anticipation of a noble metal intermediate between silver and gold, nor a set of three intermediate between palladium and platinum, but there is a greater anticipation of the rare earths, &c.

Royal Institution.—On Saturday, May 19th, at 3 o'clock, Sir James Dewar will deliver the first of a course of two lectures at the Royal Institution, on "The Old and the New Chemistry." The Friday Evening Discourse on May 18, will be delivered by Professor Arthur Schuster on "International Science."

For gadolinium, Urbain's data are as follows, calculated with $H=1.007$ and $S=32.006$:—

Fraction.	Weight $Gd_2(SO_4)_3.8H_2O$.	Weight Gd_2O_3 .	Atomic weight.
18.	1.9256	0.9350	157.35
19.	1.9749	0.9589	157.35
19.	1.9975	0.9698	157.32
20.	2.1083	1.0231	157.15
20.	1.8993	0.9214	157.04
21.	2.2065	1.0707	157.13
21.	1.9535	0.9479	157.12
22.	2.2008	1.0685	157.32
22.	2.2482	1.0914	157.28
23.	2.1932	1.0646	157.25
35.	2.0551	0.9974	157.19
36.	2.1555	1.0469	157.45
37.	2.2277	1.0807	157.04
38.	2.2559	1.0946	157.11
39.	2.2523	1.0939	157.45

Mean 157.24

The value adopted by Urbain from Fractions 18 to 23 is $Gd=157.23$.

* From the *Journal of the American Chemical Society*, xxviii., No. 3.

The paper by Brill (*Zeit. Anorg. Chem.*, xlvii., 464) describes an attempt to determine atomic weights on very small quantities of material by means of the micro-balance invented by Nernst. In each case a few m.grms. of a sulphate, previously heated to 480°, was ignited to oxide. At 480° acid sulphates were destroyed and the normal salts were stable. The results obtained may be summarised as follows:—

Yt.	Er.	Yb.	La.	Sm.	Nd.
89.7	165.6	173.2	139.5	151.2	141.8
89.5	167.5	172.2	139.8	150.5	143.0

These figures, of course, are only approximations; but they indicate the convenience of the method for the ordinary rough determinations which are needed in the identification of the earths.

Feit and Przibylla (*Zeit. Anorg. Chem.*, xliii., 202), in an investigation of the monazite earths, made several determinations of atomic weights by a volumetric method. The weighed oxides were dissolved in a known quantity of standard sulphuric acid, and the excess of the latter was ascertained by titration, with methyl- or ethyl-orange as indicator. For lanthanum, in a single experiment, the value 139.0 was found.

For neodymium and samarium the following results were obtained:—

	Nd.		Sm.
	144.51		151.20
	144.48		151.25
	144.53		151.13
Mean ..	144.5	Mean ..	151.2

Matignon (*Comptes Rendus*, cxli., 1230) has found that samarium sulphate heated to about 1000° is converted into a stable basic salt, Sm_2SO_6 . He proposes to use this transformation as a means of determining the atomic weight of samarium. In one experiment, 0.7325 gm. of $\text{Sm}_2(\text{SO}_4)_3$ calcined at a dull red heat gave 0.5335 of the basic compound. Hence $\text{Sm} = 150.6$.

According to Urbain (*Bull. Soc. Chim.*, [3], xxxiii., 403), in a communication to the Chemical Society of Paris, the following atomic weights are approximately true:—Terbium, 159.5; dysprosium, 162–163; holmium, 140. In a later paper he assigns the value 159.2 to terbium (*Comptes Rendus*, cxli., 521). For an impure terbium preparation Feit found the value 158.6 (*Zeit. Anorg. Chem.*, xliii., 280). Emma Potratz (*CHEMICAL NEWS*, xcii., 3), from a preparation of terbium sulphate, found $\text{Tb} = 153.9$, and from another sample 154.2. From the formate she obtained the figure 154, and from the acetate 153.1. No details are given, but another report is promised in the future.

Miscellaneous Notes.

From the density and critical constants of sulphur dioxide, Guye has computed its true molecular weight (*Comptes Rendus*, cxli., 1241); $\text{SO}_2 = 64.065$, and therefore $S = 32.065$. The molecular weight of argon, determined in the same way, is 39.866. Jaquerod and Scheurer (*Comptes Rendus*, cxli., 1384), from the compressibility and density of SO_2 , determine its molecular weight as 64.036, whence $S = 32.036$. Guthe (*Bull. U.S. Bureau of Standards*, i., 349), in a paper upon the silver coulometer, has discussed the electro-chemical equivalent of silver. There is also a memoir by Reuter Dahl on electro-chemical equivalents and atomic weights (*Trans. Amer. Electrochemical Soc.*, vii., 187).

Makower has attempted to determine, from their rates of diffusion, the molecular weights of the radium and thorium emanations (*Phil. Mag.*, [9], ix., 56). For the radium emanation he finds the values 85.5, 97, and 99, assuming the substance to be monatomic. The thorium emanation is but slightly different. Makower suggests that the emanation may fill the vacant place in the periodic table between molybdenum and ruthenium. The atomic

weight of radium itself has been discussed by Jones (*Am. Chem. Journ.*, xxxiv., 467), who, from a critical examination of all the evidence, is inclined to favour the higher of the two rival values, namely, $\text{Ra} = 258$.

On the calculation of atomic weights, there is an interesting paper by J. Meyer (*Zeit. Anorg. Chem.*, xliii., 242). An important suggestion by Luther (*Zeit. Elektrochem.*, xi., 273) is to refer combining weights, through the aid of Faraday's law, to the C.G.S. system of units. In this way the question of standards might be settled and a rational table devised.

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

PART II.—ANALYSIS OF THE TUNGSTEN GROUP.

By ARTHUR A. NOYES.

(Continued from p. 207).

Test Analyses.

At different stages in the development of the process above described, numerous analyses were made to test its efficiency. Nearly all of those which were made after integral parts of the procedure assumed final form are reproduced in the tables below. In these tables the numbers in each vertical column show the weights in m.grms. of the various elements which the solution submitted to analysis contained. The results of the tests for each element are shown by the letters following these numbers. That the result was satisfactory is indicated by the letter S; that is, when the element was present, that the test for it, however small, was unmistakable and therefore conclusive; and when the element was absent, that a good blank test was obtained. When the test was very small in comparison to the quantity of the element present, though still unmistakable, or when in its absence (especially in the niobium and tantalum tests) there was obtained not a perfect blank but yet one good enough to warrant the conclusion that less than one m.grm. is present, this is sometimes indicated by the symbol S—. When in the presence of the element the test failed, or in its absence a result was obtained that might be thought to indicate its presence, the letter F is used. When the result was doubtful or inconclusive, owing, for example, to the test being obscured by some other element, this is indicated by the letter D. When the test was not tried, if the element was present, a dash is used in place of a letter, or, if the element was not present, the whole space is left blank.

The first series of twenty-three analyses were made by Mr. D. P. Smith, at a time when the procedure through the analysis of the titanium, tantalum, and niobium hydroxide precipitate was in nearly its final form, but when the tin and tungsten were still being separated by heating the moist, precipitated sulphides with strong hydrochloric acid. Therefore, owing to the solubility of tungsten sulphide under these condition (see G. D., § 10), the failures to detect tungsten in the presence of much tin in these analyses do not show a defect in the final procedure. In all of the analyses of this series, before testing for tungsten, the sodium carbonate solution (P. 40) obtained from the filtrate from the sulphuric acid precipitate was united with an ammonia solution of the residue left upon treating the sulphides with nitric acid (P. 43), and the mixed solutions were then evaporated with nitric acid to separate the yellow tungstic acid. The results given for the niobium tests are always those obtained in the second test with mercuric chloride after the fusion with sodium carbonate and sulphur, when a precipitate obtained in the first test made this fusion necessary.

A second series of analyses (Nos. 24–29) were made by Mr. F. M. Eaton, who had no previous experience in con-

* From the *Technology Quarterly*, xvii., No. 3.

FIRST SERIES.

T. A. No.	1 (a)	2	3	4	5	6	7	8
Analysis begun at P...	3	3	3	33	33	33	33	33
Ta	0 S	0 S	2 F	2 S	2 S			2 S
Ti	500 S	100 S	300 S	300 S	300 S	300 S	300 S	300 S
Nb	0 S	0 S	1 F			0 S—	0 S	0 S—
Sn	1 F	1 S	300 S	3 S	300 S			2 S
W	1 F	2 S	1 F	300 S	5 F	300 S	5 S	300 S

T. A. No.	9	10	11	12	13	14	15	16
Analysis begun at P...	33	33	33	33	33	33	33	5
Ta	0 D (b)	2 S	0 S—(b)		2 S	100 S	2 S	2 S
Ti	300 S	3 S	300 S	200 S	300 S	2 S		2 S
Nb	2 F	0 S	5 S	2 S (c)		2 S (c)	100 S	0 F (d)
Sn	300 S	300 S	300 S					
W	2 F	300 S	5 F					3 F (e)
Mo								500 S

T. A. No.	17	18	19	20	21	22	23
Analysis begun at P...	31	33	33	33	33	33	33
Ta							
Ti	300 S	5 S		5 S	300 S	300 S	300 S
Nb	0 S		5 S				
Sn		300 S	300 S				
W				300 S	5 F	5 S	10 S
Mo	300 S						

SECOND SERIES.

T. A. No.	24	25	26	27	28	29
Analysis begun at P...	31	31	31	31	31	33
Sb	3 S	2 S	1 S	3 S		
Ta	3 S	2 S	1 S	3 S	0 S	2 S
Ti	3 S	1 S	1 S	3 S	2 S	300 S
Nb	3 S	2 F	1 S—(h)	3 S	2 F (i)	0 S (g)
Sn	3 F	2 F	1 F	3 S	2 F	2 F
W	3 F	300 S	1 F	3 S (f)	2 F	2 F
Mo					300 S	

THIRD SERIES.

T. A. No.	30*	31*	32*	33*	34	35	36	37*	38	39
Analyst	D. P. S.	F. M. E.	F. M. E.	F. M. E.	D. P. S.	D. P. S.	D. P. S.	F. M. E.	D. P. S.	D. P. S.
Analysis begun at P...	31	31	33	31	31	31	31	31	31	35
Sb	0 S	400 S		0 S			400 S			
As	2 S			2 —					100 S	
Ta	0 F	0 D (k)	2 S—(l)	2 S	0 S	0 D (b)	2 S	2 S	0 S	
Ti	2 S	2 S	400 S	400 S	2 S	400 S	2 S	2 S	2 S	400 S
Nb { First test .	S	S	F	F	S	F	S	S	S	F
Second test	—	S	S	S	—	F (d)	F	F	—	S
Sn	400 S	2 F	2 F	4 F	2 F	4 F	4 S	4 F	400 S	
W { P. 40.. ..	F	F	S	S—	S	F	S	F	F (m)	
P. 43.. ..	—	F	4 S—	400 S	4 F	4 F	4 F	4 S—	4 F	
Mo		0 S	2 S	2 S	400 S	400 S	2 S	400 S		200 S

FOURTH SERIES.

T. A. No....	40	41	42	43	44	45	46	47
Analyst	D. P. S.	D. P. S.	D. P. S.	F. M. E.	F. M. E.	F. M. E.	F. M. E.	D. P. S.
Analysis begun at P.	33	33	33	35	31	35	35	35
Sn	300 S	300 S	1 S	30 S	8 S			
W { P. 40	—	—	—	S (n)	—	—	F	—
P. 43	3 S	1 S	300 S	8 F	8 S	4 S	2 S—	2 F
Mo		—			400 S	100 S	100 S	100 S
PO ₄		—		20 S				

nection with this process, and who was given no information in regard to it other than that contained in a copy of the "Procedure and Notes." The procedure was then in final form, except that the hydrochloric acid solution of the ignited sulphides was tested for tin by adding it directly to mercuric chloride, instead of first reducing it with zinc, which accounts for the repeated failures to detect small quantities of tin (see P. 42, N. 1). The results with niobium were those obtained in the second mercuric chloride test after the fusion with sodium carbonate and sulphur, except where otherwise indicated by foot-notes. The sulphuric acid precipitate and the filtrate from it were separately tested for tungsten.

The third series of analyses (Nos. 30—39) were made according to the final procedure in every respect, in part by Mr. D. P. Smith and in part by Mr. F. M. Eaton, as indicated by the initials at the head of the columns. As a matter of information, the results of both the first and second mercuric chloride tests for niobium are recorded, but it is only the second one that is really significant of the presence or absence of that element, except when the first test gives a negative result. The results of testing for tungsten both the sulphuric acid precipitate (by P. 41 and 43) and the filtrate from it (by P. 40) are also shown, but the detection of it in either place is, of course, a satisfactory result. In those analyses to the numbers of which a star is attached the contents of the mixture were unknown to the analyst in advance. Such unknown mixtures were not analysed in greater number, because to a person having any experience with the process the interpretation of the tests is scarcely ever doubtful; and as long as the procedure is in process of development, it is advantageous that the analyst know immediately of failures to secure the right result.

The fourth series of analyses (Nos. 40—46) were also made after the procedure was fully developed, but they have reference only to the detection of tin, tungsten, molybdenum, and phosphate in the presence of one another.

In order to summarise the results of these analyses, and form thereby a judgment in regard to the efficiency of the procedure, each element will be considered separately.

Notes to Table.

- (a). This mixture also contained 1 m.grm. Sb and 1 m.grm. Mo, and these were detected in the H_2S precipitate.
- (b). A small precipitate (very slight in T. A. 11) was obtained, owing to a little tantalum in the titanium used. To show the presence of this impurity, 400 m.grms. Ti were alone put through P. 33, 35, and 36; a precipitate corresponding to that given by 2 m.grms. Ta was obtained.
- (c). This was the result even after the fusion with Na_2CO_3 and S, which was made to see whether it would result in loss of the niobium.
- (d). In this analysis the $(NH_4)_2S$ precipitate was not redigested with NH_4OH , as directed in P. 35, when much molybdenum is present.
- (e). H_2SO_4 was not used, as directed in P. 43, to cause the tungsten to separate.
- (f). Tungsten was detected only in the filtrate.
- (g). Fusion with Na_2CO_3 and S was omitted, since no precipitate formed in first $HgCl_2$ test.
- (h). Fusion with Na_2CO_3 and S was omitted, since the precipitate in first $HgCl_2$ test was too slight.
- (i). There was a very slight turbidity in the first $HgCl_2$ test.
- (k). A light, flocculent precipitate separated on standing.
- (l). A light, flocculent precipitate first separated; but upon repeating the treatment of P. 36, it assumed the characteristic appearance of the tantalum precipitate.
- (m). The reduction test with Zn at end of P. 40 was not tried, which may have been necessary, since the

arsenic, if present in this solution, would have prevented the separation of tungstic acid.

- (n). No yellow H_2WO_4 separated, but a decided blue coloration was obtained with Zn.

(To be continued).

A REVISION OF THE ATOMIC WEIGHTS OF SODIUM AND CHLORINE.*

By THEODORE WILLIAM RICHARDS

and
ROGER CLARK WELLS.

(Continued from p. 203).

THE OCCLUSION OF DISSOLVED SUBSTANCES BY ARGENTIC CHLORIDE.

It is well known that all precipitates have a tendency to carry down with them other substances from the solution in which they are formed (Jannasch and Richards, *Journ. Prakt. Chem.*, 1889, xxxix., 321; Schneider, *Zeit. Phys. Chem.*, 1892, x., 425; Richards, *Proc. Amer. Acad.*, 1900, xxxv., 377; *Zeit. Phys. Chem.*, 1903, xlv., 189). According to the nature of the precipitate, the mechanism of this contamination varies. A basic precipitate such as ferric hydroxide is likely to carry down traces of acid in the form of basic salt; an acid precipitate such as silica is likely to carry down traces of base; many substances are contaminated in the act of precipitation by the admixture of isomorphous substances in solid solution; all or nearly all crystals contain within themselves minute cells inclosing mother-liquor, and very finely divided precipitates, because of their large surface, pertinaciously adsorb in varying amount impurities from the supernatant solution. Obviously contamination from any of these sources must be scrupulously avoided in accurate work, and the peculiar qualities of each precipitate under investigation must be studied.

As has been said, argentic chloride was known by Stas to occlude argentic nitrate, which is easily detected by its blackening effect upon fusing the contaminated chloride. (Richards, *Proc. Amer. Acad.*, 1893, xxix., 76. The blackening occurs in full measure only when the argentic nitrate is occluded from aqueous solution. Perfectly dry argentic nitrate fused with dry chloride is but slightly decomposed, and the fused mass is merely grey, not black. The probable explanation is obvious). This test is a delicate one. Stas found that upon working with solutions of argentic nitrate weaker than decinormal, the occlusion was so slight as to be negligible; therefore in his early experiments he took great pains never to use solutions stronger than this. Later, he seems to have overlooked this precaution, since he used much more concentrated solutions. Although realising that argentic nitrate is occluded by the precipitate, Stas seemed never to have guessed that other salts might also be taken up in this way. Evidently the question was one which needed further investigation, and the outcome of the investigation is recorded below.

It was convenient at first to determine whether or not the occlusion of sodic nitrate or sodic chloride would also affect the appearance of the silver salt on fusion, in order to discover an easy qualitative test for the presence of either. As a matter of fact, the former salt was found by actual admixture to colour the fused silver chloride a pale buff, rendering it opaque; while the latter had no perceptible effect upon its appearance. Thus Stas could not have detected the presence of sodic chloride in his precipitate by the appearance, whether fused or unfused. An impurity of argentic nitrate being thus the most easily detected among the possible impurities, the next step was

* Published by the Carnegie Institution of Washington, April, 1905.

to use the contamination with this salt as a means of testing the properties of the precipitate.

It was early found that upon shaking pure argentic chloride with a solution of argentic nitrate, the latter is adsorbed upon the surface of the precipitate. If a solution containing argentic nitrate and the curdy precipitate is divided into two equal volumes, one containing the precipitate and one clear, and if the precipitate is then carefully washed, more argentic nitrate will be found in the portion which contained the precipitate than in the other portion. A further evidence of this adsorption is found in the fact that the theoretical amount of washing is especially inadequate to remove the last traces of adhering electrolyte.

These experiments show not only that the nitrate is adsorbed, but also that some at least of the adsorbed salt may finally be washed off.

In view of this result, it seemed probable that the reason why silver chloride occludes silver nitrate in the act of precipitation is because the former adsorbs the latter during this process, and the adsorbed material is then covered up by newly-formed precipitate. The more dilute the precipitating solutions, the less considerable would be the adsorption.

The peculiar curdy, flocculent form of this precipitate suggested that since the material is so flexible, long-standing and gentle agitation with pure water might allow the occluded material to escape, although from a more rigid precipitate this escape is known to be impossible. With this possibility in view, a number of experiments were made in the following manner:—Argentic chloride was precipitated from several portions of a concentrated solution of the nitrate, thus occluding much (in some cases as much as 0.1 per cent) of this salt. The effort was then made to wash these precipitates; and the possibility of thorough washing was found to vary greatly with the treatment of the precipitate. In those cases where the precipitate had remained for two or three days in contact with a mother-liquor rich in silver, it was found much more difficult to remove the nitrate than in cases where the washing was more prompt. It seems as if the innermost cells of the precipitate are closed upon standing during the well-known contraction which then occurs. In one case where normal solutions had been used in precipitation, six prompt, gently-agitated washings with pure water were enough to remove practically all the occluded material, and yield a chloride which fused without blemish; but this praiseworthy behaviour was the exception rather than the rule. In this case the innermost cells must have been cleaned before they closed during the compacter aggregation of the precipitate; but usually traces of silver nitrate were enclosed, and when they were once enclosed were beyond the reach of even a dozen washings. Therefore more dilute solutions of argentic nitrate were used in precipitating, in order to find the limit beyond which a satisfactory precipitate was certain. Third normal solutions were found to be still slightly too concentrated, but fifth normal solutions always yielded a satisfactory result, if speedily but gently washed six times, and then occasionally agitated in pure water in order to dissolve out the last trace of nitrate. In previous determinations in this laboratory still less concentrated solutions (tenth normal) were used, so that no correction need be applied to those determinations on this account. (See, for example, Richards, *Proc. Amer. Acad.* 1893, xxix., 76). This further dilution is necessary unless the curdy precipitate is speedily washed or agitated with a solution containing no excess of silver.

Having thus obtained light on the mechanism of the occlusion of argentic nitrate, we turned our attention to the possibility of occluding sodic chloride. Here, as had been said, no qualitative experiment can conveniently prove the presence of the impurity. Hence recourse was had to a quantitative experiment. An amount of pure salt known by previous experiment with very dilute solutions to be exactly equivalent to a given weight of pure silver

was carefully weighed out, and the solid was dropped into a fairly concentrated solution of the nitrate, according to Stas's later method of procedure. After two hours' thorough shaking and a day's standing, which Stas had always given, it was found that 0.014 per cent more of salt had to be added in order to attain exact equivalence, showing that this amount of salt remained occluded by the precipitate even after the shaking and standing. Agitation for another day leached out about one-half of the occluded salt, but seven days' soaking and agitation were required before the full amount (0.014 per cent) of extra silver nitrate was needed to attain equivalence with the salt dissolved out of the precipitate. Subsequently, in several days no more salt appeared; hence the final condition must have been reached. Since probably some silver nitrate also was occluded, it is clear that these figures represent a minimum value, and the certain error introduced by Stas's method of procedure was demonstrated. The reason why he obtained consistent results was simply because he used exactly the same method in each analysis.

Obviously, then, a solid salt is not to be dropped into a precipitating solution—indeed, such a proceeding is so repugnant to the instinct of a precise quantitative analyst that it is surprising Stas should have been guilty of it. But how dilute must the precipitating sodic chloride be in the present case in order to avoid the danger? Careful experiments showed that with fifth normal solutions, as in the case of silver, such slight occlusion as existed was quickly removed by gentle agitation, and after a short time the mixture showed a constant equilibrium point. Hence in our final experiments the solution was always as dilute as this. In previous similar work in this laboratory, the solutions of halide were rarely stronger than fifth normal, and never much stronger, so that the error from this source must have been very small.

It might be supposed that when the sodic chloride and argentic nitrate are too dilute to be carried down with the precipitate, sodic nitrate is not likely to be carried down in important amounts. For if both silver and chloride are fifth normal, the resulting sodic nitrate must be tenth normal, a dilution at which even silver nitrate is not sensibly occluded. Nevertheless, as a matter of fact, the final experiments yielded quantitative evidence of the occlusion of a trace of this salt, amounting to 0.005 per cent of the weight of the precipitate. This is probably because the precipitate was obliged to stand for some time in the solution, and it is doubtful if this source of error could be wholly avoided.

From these experiments it appears that the degree of dilution at which occlusion ceases to be seriously troublesome is about the point at which most physical chemists agree that the realm of dilute solutions begins. Hence it would seem that in these cases of adsorptive occlusion the undissociated salt is that which is occluded, in confirmation of other work (Richards, MacCaffery, and Bisbee, *Proc. Amer. Acad.*, 1901, xxxvi., 377).

Obviously the occlusion of argentic nitrate, or of sodic chloride, would affect the results of the analysis, no matter whether silver or argentic chloride served as the weighed standard wherewith to compare the weighed sodic chloride, although more seriously in the former case than in the latter. On the other hand, the occlusion of sodic nitrate could only affect the result when the argentic chloride was weighed; its occlusion would have no effect on the amount of silver required to precipitate the chlorine. The possible effect of these disturbing influences will be alluded to again during the recital of the quantitative operations.

It is needless to say that these experiments were carefully carried on in complete darkness, in order to avoid the known disturbing effect of photochemical action. The temperature was usually 20° C. Undoubtedly this condition is important, since the aggregation of argentic chloride is greatly affected by change of temperature.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, April 27th, 1906.

Dr. C. CHREE, F.R.S., Vice-President, in the Chair.

MR. W. B. CROFT read a paper on "*Some Simple Questions on the Images of Microscopes and Telescopes.*"

It may have been noticed that when a microscope is focussed visually, an image is formed on the focussing-glass of a camera, into which the microscopic eye-piece is inserted after removing the camera-lens. This image remains more or less in focus at variable positions of the camera-screen. Although it is not always perhaps true, yet it is surprising how often the pencil emerging from a microscope eye-piece behaves like a single concentrated line of light. A mounting of the proboscis of a fly was focussed visually, then a camera was put on the end of the microscope, and the screen was racked out to six positions over a range of about six inches. At these positions six photographs were taken, of which the two smallest pictures were inferior to the others. It was claimed that this defect was due to imperfect exposure and uneven illumination. If the visual focussing had made pencils slightly diverging instead of parallel, the larger pictures should have been the more imperfect. These pictures were obtained with a 1-inch objective. Next, a diatom, *Triceratium favus*, was photographed with a $\frac{1}{2}$ -inch objective. With a visual focussing two photographs at different distances were taken; these were similar to one another and to what was seen. The same diatom then had a slightly different visual focussing, with the same result as before in the two pictures. Finally, two diatoms with fine markings were focussed visually and at two positions; the markings came out clearly in the photograph. The object of showing the results was not to make out that the emergent pencil was ever actually, or always approximately, a single line of light, but to intimate how often the author had found, when projecting from an optical eye-piece, that no change can be detected in the definition of the image as the screen of the camera is moved. If a camera-lucida is placed on the eye-piece, the image of a stage-micrometer can be thrown on a scale at 10 inches distance or at 40 inches distance. The parallel rays emerging from the eye-piece give the image of a point along a direction, at no definite position. The image can be imagined at 40 inches distance as easily as 10 inches.

Mr. CROFT also showed some photographs taken from sections of the human eye; he indicated that a divergent pencil from a small aperture or from a convex reflecting surface of large curvature will give the Purkinje figures as bright radiating lines, whereas the usual method of sending light through the side of the sclerotic gives them as shadows.

Several different specimens were shown of magnetic oxide of iron and magnetic sulphides of iron. The power of nickel and cobalt to receive permanent magnetism was illustrated with a compass-needle of nickel.

Mr. A. P. TROTTER, referring to the fact that when taking microscopic photographs the screen could be placed at any distance from the eye-piece of the microscope, pointed out that this was not the case when using an astronomical telescope, the screen having to be placed in a definite position to obtain a sharp focus.

Prof. H. L. CALLENDAR, referring to the fact that when the microscope used in the author's experiments was focussed visually, it also formed sharp images on a screen at any distance, suggested that this might be due to some peculiarity in the eye of the observer.

Mr. C. V. BOYS gave a demonstration of the construction and action of his gas calorimeter described in the *Proceedings of the Royal Society* for January, 1906.

This is the instrument which is being used for testing the calorific value of London gas under the provisions of the London Gas Act, 1906.

Mr. J. MORROW read a paper "*On the Lateral Vibration of Bars Subjected to Forces in the direction of their Axes.*"

In the paper a statement of the general problem of the lateral vibration of rods is first made. The rods are assumed to be subjected to an axial tensile or compressive force, and the differential equation given may be applied to bars of uniform or varying sectional area, and to cases in which the bar carries one or more loads concentrated at different points in its length. In considering any special problem we may either start with this general equation, or we may write out a particular differential equation suitable to the conditions of the case in question only. Three cases of unloaded bars are dealt with, namely, those under the following end-conditions—"supported-supported," "clamped-clamped," and "clamped-supported." Expressions are obtained from which the frequencies may be calculated, and the results are stated in a form such that the determination of stresses, terminal couples, &c., may be easily made. The case of greatest interest is that of a stretched bar clamped at each end. Approximate solutions of this problem have been arrived at by both Seebeck and Donkin. These are on the assumption that the vibration is but slightly affected by the rigidity of the material. An assumption of a very different character, and one generally fulfilled in structural work, is made in this paper, namely, that the longitudinal force is not very great. Solutions are thus found for the period of the fundamental or any harmonic. Two other methods are applied to the solution of the same problem. These are the method of successive approximation, and the approximate "energy-method" of Lord Rayleigh. Both these methods are free from the assumptions mentioned above, and give results closely agreeing with that first obtained. These results may be applied in problems of long struts or tie-rods as distinct from the long and fine wires of acoustics. The cases next dealt with are those of bars of negligible mass, carrying a concentrated load, and subject to longitudinal force. Expressions are obtained for the curve of the bar at any instant, the couples at the end and the periods of vibration. It is found throughout that, when the axial force is compressive, there is a certain limiting load at which vibration ceases. The amount of this load varies with the conditions at the ends of the rod, and the expression for it agrees with that given by Euler for the elastic stability of a long column. The paper closes with an application of the solutions to some static problems of loaded beams. By a simple change of notation the expressions for the displacements of such bars replace those for the types in the vibration problems. Several results not hitherto recorded may be so obtained.

FARADAY SOCIETY.

Ordinary Meeting, April 10th, 1906.

Prof. A. K. HUNTINGTON in the Chair.

MR. F. W. HARBORD communicated to the meeting papers by Messrs. Keller, Stassano, and Gin. The paper by CH. A. KELLER was entitled "*Electrothermics of Iron and Steel.*"

The author deals with the present position of his processes; he describes the electrical steel plant which Messrs. J. Holtzer and Co. have just installed in their works at Unieux (Loire). This is a 1500 H.P. plant, and will utilise in a single furnace the current from a 20,000 ampère Westinghouse alternator. The furnace, which rests on a steel cradle and can be tilted, weighs about 50,000 kilos.; the various mechanical and electrical controls are obtained by hydraulic motors. The steel

obtained from a Siemens-Martin furnace will be run into the electric furnace immediately after the oxidising melt, and for the remaining operations of deoxidising and refining, the current exclusively will be used. It will be possible to operate on 8000 kilos. of metal at one time, and the operation will be repeated three or four times in the twenty-four hours. The steel produced by this furnace is intended for cannon and projectiles. The author promises at a future date to furnish details of the results obtained.

Some experiments made at Livet comparing the metal obtained in a 1000 H.P. Keller furnace with that obtained in the blast-furnace are further described, and curves are given showing the proportions of carbon and silicon in castings produced in both ways. It appears that the Keller furnace allows of ready desulphurisation and of easier variation in the proportions of the above elements than does the blast-furnace; it would thus be advantageous for the production of soft castings and castings for mill work. Tests on some of these electrothermic castings are described.

The author has just set up at Livet a 2000 H.P. furnace utilising a current of 25,000 ampères, and capable of producing 20 tons of castings in twenty-four hours. This will be used specially for the industrial working of the process. Further details respecting the new furnace are promised.

Mr. W. MURRAY MORRISON referred to the freezing of the metal in the central passage in the first furnace that had been erected, and asked for further information regarding the easy variations in silicon content claimed by the author.

Mr. F. W. HARBORD said the freezing trouble was probably only due to the special conditions of the first tests recorded, and in any case could be avoided by coupling two or four furnaces together. Regarding variation of silicon content, as a rule this was easily brought about by adding a little silicon pig, but it might conceivably, under special circumstances, be useful to vary it in the way described for the production of good castings.

Prof. A. K. HUNTINGTON described some experiments he carried out in 1881 with the Siemens electric furnace in which he was able to vary the silicon content from $\frac{1}{4}$ to 9 per cent. He had also succeeded in volatilising copper and in making solid tungsten.

The paper contributed by Cav. Megg. ERNESTO STASSANO was entitled "*Note on the Rotating Electric Steel Furnace in the Artillery Construction Works, Turin.*"

The furnace described and illustrated in the paper is being installed by the "Forni Termoelettrici Stassano" Company for the Italian War Office. It is of the author's well-known arc type, and absorbs 140 kilowatts yielding 2400 kilos. of steel in twenty-four hours. The current is a rotary one with 80 volts between each phase. The consumption of electrodes is under 5 kilos. per ton of steel, and the cost of renewing the refractory covering of the furnace 10 francs per ton of metal made. The furnace is principally used for refining pig-iron and smelting scrap. The product ordinarily made is used for artillery projectiles.

Mr. F. MURRAY MORRISON thought the efficiency would not be so great as with the Keller or Héroult type.

Prof. A. K. HUNTINGTON asked whether there would not be greater consumption and wear of electrodes if they were touching. He did not consider the process offered any special advantages for ordinary steel making.

Dr. H. BURNS asked whether Stassano always used very pure iron ore from Elba and other Italian mines.

Mr. CHARLES WEISS pointed out that the paper did not state whether steam or water power was used in the Turin Works. He thought that in countries like South America, where water power was available and there was plenty of rich ore, it might be useful to smelt copper ores in the electrothermic furnace.

Mr. F. W. HARBORD said the efficiency as stated was somewhat greater than in the other furnaces. For special castings there might be advantages in heating by radiation

only. The figures given for carbon consumption were smaller than in the Keller or Héroult furnaces. He thought the rotation was the weak point in the furnace.

With regard to the general question of electric steel smelting, a maker had recently told him that he had sold 300 tons of such steel as crucible steel, and the buyers were so pleased with it that they were asking for more. That was strong evidence that good steel could be made in the electric furnace, but it was only high-priced steel that could be commercially made (in England) by such means.

Mr. Harbord then read M. GUSTAVE GIN'S "*Note on Recent Developments in the Gin Electric Steel Furnace.*"

The author's canal type of furnace is now installed at the Plettenberg Works, Westphalia, of which illustrations are given in the paper, but it is not stated which particular type of furnace has there been experimented with. The following types are described:—

1. *Furnace with Canals and Chambers.*—Unlike in the canal form originally suggested, the electrothermic heating and refining now take place separately, the latter in chambers which communicate with each other and with the leads by the canals, now used exclusively for heating. The construction of a 7200 kilowatt furnace, utilising 60,000 ampères at 120 volts and designed to yield over 350 tons in the twenty-four hours, is described in detail. The author claims that the furnace combines the advantages of the Martin and Talbot furnaces, the separation of the operations making exact control of composition possible.

2. *Combination Furnace.*—This consists of a melting and oxidising crucible, a deoxidising and re-carbureting compartment, and a final mixing chamber, and is fully described and illustrated in the paper.

3. *Induction Furnace.*—The author's suggestions for various types of induction furnace are described. The use of multiple canals is proposed, so that if steel is being produced, oxidation can be carried out in one canal and reduction in the other. In another suggested type, more intimate circulation and mixing of the product is brought about by means of lateral conduits connecting the respective ends of the open flues of which the channel crucible is made up.

The paper by Mr. H. S. COLEMAN entitled "*Notes on the Cleaning of Work by means of the Electric Current*" was communicated by Dr. F. MOLLWO PERKIN. (See p. 167).

ROYAL INSTITUTION.

Annual Meeting, May 1st, 1906.

THE DUKE OF NORTHUMBERLAND, K.G., in the Chair.

THE Annual Report of the Committee of Visitors for the year 1905, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy-Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read.

Forty-five new Members were elected in 1905. Sixty-three Lectures and nineteen Evening Discourses were delivered during the year. The Books and Pamphlets presented amounted to about 254 volumes, making with 697 volumes (including Periodicals bound) purchased by the Managers, a total of 951 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Sir William Crookes.

Managers—Sir William de W. Abney, The Rt. Hon. Lord Alverstone, The Rt. Hon. Earl Cathcart, Dr. A. H. Church, Dr. F. Elgar, Dr. D. W. C. Hood, Mr. M. Horner, Sir William Huggins, The Rt. Hon. Lord Kelvin, Mr. H. F. Makins, Dr. Ludwig Mond, Sir R. Douglas Powell, Bart., The Rt. Hon. Lord Sanderson, Mr. Alexander Siemens, and the Rt. Hon. Sir James Stirling.

Visitors—Dr. J. Mitchell Bruce, Mr. Dugald Clerk, Sir John George Craggs, Mr. H. Cunynghame, Mr. G. F. Deacon, Mr. E. Dent, Rev. J. H. Ellis, Mr. R. K. Gray, Mr. C. E. Groves, Mr. F. G. Henriques, Mr. A. C. Ionides, Mr. C. E. Melchers, Mr. E. R. Merton, Mr. H. Swithinbank, and Mr. G. P. Willoughby.

NOTICES OF BOOKS.

Chemical Analysis, Qualitative and Quantitative. By WILLIAM BRIGGS, LL.D., M.A., B.Sc., F.C.S., and R. W. STEWART, D.Sc. (Lond.). Fifth Impression (Fourth Edition). Revised and Enlarged by H. W. BAUSER, M.A. London: W. B. Clive. 1906.

THE fourth edition of this text-book of chemical analysis gives a good collection of group tests, with clear systematic tables, and a useful set of model analyses. It also contains a sketch of gravimetric and volumetric work, sufficient to cover the syllabus for the London Intermediate Science and Preliminary Scientific Examinations. The directions for the analysis of both simple salts and mixtures appear to be clear and adequate, and the student who works through the book should find no difficulty in passing in chemistry in the above examinations; whether he will have been thought to think is another matter. As a book designed especially for the use of examination candidates it certainly fulfils its purpose.

A Three Years' Course of Practical Chemistry. By GEORGE H. MARTIN, M.A., F.C.S., and ELLIS JONES, M.A. Third Year. London: Rivingtons. 1906.

IN the third part of this course of practical chemistry the properties and reactions of a few of the most important non-metallic elements are thoroughly studied, and useful sets of questions are included, special stress being laid upon chemical arithmetic. The general plan is the same as that adopted in the first and second parts, and it seems to have been equally well worked out, the greater part of the experimental work being done by the students themselves, although there are necessarily a good many experiments which are better suited for demonstration. The pupil who works through this course of chemistry should acquire a very good insight into the elements of the science, and lay a thoroughly sound foundation for further work.

An Introduction to Chemical Crystallography. By P. GROTH. Authorised Translation by HUGH MARSHALL, D.Sc., F.R.S. London: Gurney and Jackson. 1906.

THIS short treatise on chemical crystallography gives a very brief review of investigations of the relations between the properties of crystalline substances and their chemical constitution. The author summarises the isolated relationships which have been detected, with the hope of thus leading up to the discovery of some general law, and, without going very deeply into the various views which have been put forward from time to time, gives a very concise and accurate statement of the most important aspects of the subject. The translation has been very carefully done, the original being closely followed, while, for the benefit of English students who cannot read German or get access to the original papers, some additional

references have been given to abstracts or translations of them in English.

Grundriss der Elektrochemie. ("Outlines of Electrochemistry"). By DR. HANS JAHN. Second Edition. Wien: Alfred Hölder. 1905.

THE second edition of this text-book of electrochemistry has been almost entirely re-written by the author, but its general character remains unaltered, and the changes in it relate chiefly to work which has been done in the last ten years. The views of Arrhenius are adopted as the basis of the book, and the treatment is mainly mathematical, the author believing that a thorough knowledge of the calculi and skill in using them to be absolutely indispensable to the chemist nowadays. He also lays stress upon the importance of physical methods especially in electrochemistry, and he endeavours to overcome the distrust which chemists sometimes exhibit towards such methods. Some parts of the book are exceedingly difficult to read, and it is hardly one that could advantageously be used by the average student, though it gives a very full exposition of the mathematical theory of electrochemistry.

La Double Réfraction Accidentelle dans les Liquides. ("Accidental Double Refraction in Liquids"). By G. DE METZ. Paris: Gauthier-Villars. 1906.

THIS monograph gives a very good summary of the actual state of our knowledge of the phenomenon of double refraction in liquids. The author discusses the means of producing this phenomenon, and describes the most important parts of his own experimental work, besides that of Kerr and Maxwell; the chapters on theoretical views are perhaps a trifle obscure in some respects, but on the whole a difficult subject is skilfully treated, and in the discussion of the constitution of colloids Bütschli's work is excellently reviewed and illustrated. The account of the discovery of Kerr's phenomenon is very clear, and the question of its identity with the phenomenon of double refraction artificially produced mechanically is lucidly treated. The author shows discrimination in the discussion of the work of different physicists, and without descending to minute detail, he manages to convey to the reader a clear idea of the main aspects of this branch of electric optics, and those who are working on the subject will find much in the book to suggest fresh experiments and new ways of attacking the problem, which may lead to the discovery of the real nature of liquids. The author has for some time devoted himself to the study of the question, and has arrived at some interesting results which are here given in full.

Analyse des Métaux par Electrolyse. ("The Analysis of Metals by Electrolysis"). By A. HOLLARD and L. BERTIAUX. Paris: H. Dunod and E. Pinat. 1906.

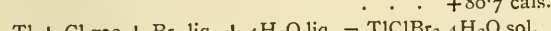
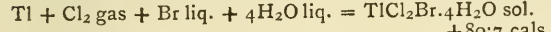
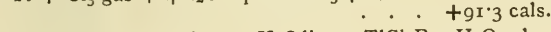
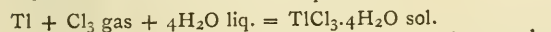
THE special object of the authors of this book has been the description of electrolytic methods of determination in those cases in which gravimetric or volumetric processes are inconvenient or wanting in accuracy; for this purpose they have analysed many mixtures of known proportions, and are thus enabled to report definitely on the degree of accuracy that may reasonably be expected in the use of electrolysis. This alone gives a value to the book, which also contains full practical details of the various methods of separation and estimation, and a scheme of classification of the metals for analytical purposes. One section is devoted to an account of general methods of analysing ores, minerals, alloys, and impure metals. Although an attempt is made to provide a general explanation of the complex phenomena of electrolysis as applied to analysis, the work is chiefly of a practical nature, and, generally speaking, the information given seems to be sufficiently full, while the alloys and minerals treated of have been carefully selected so that they represent the most typical and important of such substances.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 14, April 2, 1906.

Halogen Compounds of Thallium.—V. Thomas.—The author makes a series of researches on the thermochemistry of the halogen compounds of thallium and on the chloruration of thallous chloride. The numbers obtained confirm the chemical existence of the thallic chlorobromides. From the series of equations—



it is seen that the successive replacing of the bromine atoms of the bromide by chlorine atoms evolve practically the same quantity of heat; the first evolving 11.0 cal., the second 10.7 cal., and the third 10.6 cal. When chloruration takes place with excess of chlorine, the process stops when all the thallous chloride is transformed into Tl_2Cl_3 . If chloruration takes place at ordinary temperatures, the bichloride, Tl_2Cl_4 , is always formed. It is necessary, however, to avoid any trace of moisture, as the bichloride is very hygroscopic, and when hydrated rapidly absorbs more chlorine, forming the hydrated thallic chloride. At a high temperature complete chloruration never takes place. If a sealed tube is used under a pressure of six or seven atmospheres, small quantities of the anhydrous chloride are formed in the form of a white sublimate.

No. 15, April 9, 1906.

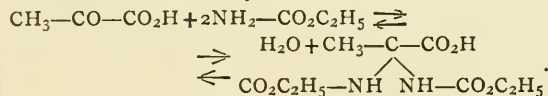
Pyrophosphoric Compounds.—J. Cavalier.—The recognised general formula for pyrophosphoric acid is $\text{P}_2\text{O}_7\text{H}_4$, which is a tetrabasic acid. There exist four sets of salts, the majority of metallic pyrophosphates having the formulæ $\text{P}_2\text{O}_7\text{M}_2\text{H}_2$ and $\text{P}_2\text{O}_7\text{M}_4$, the mono- and tri-metallic salts being rarer and less definite. The existence of the latter, however, has been proved. The author now prepares the neutral pyrophosphates of ethylic, normal propylic, isopropylic, normal butylic, amyl, and allylic alcohols. The pyrophosphoric ethers are liquid, with an odour resembling the corresponding ortho-phosphates. They decompose with heat, and can be distilled; they are soluble in benzene, carbon disulphide, carbon tetrachloride, and ether. The ethylic compound is soluble in water, the liquid formed being strongly acid.

Barium Iodo-mercurates.—A. Duboin.—The author prepares a saturated solution of barium iodo-mercurate by the same method as that used to prepare calcium and strontium iodo-mercurates. On analysis its composition is found to be—Ba, 12.14 per cent; mercury, 23.32 per cent; iodine, 52.05 per cent; from which the formula $\text{BaI}_2 \cdot 1.33\text{HgI}_2 \cdot 7.76\text{H}_2\text{O}$ can be deduced. This is evidently a mixture of two iodides soluble in alcohol at 96°, the saturated solution having for its density 2.76 at 23.5°. The author also obtains another definite hydrate at -9°C., having the composition $\text{BaI}_2 \cdot 1.30\text{HgI}_2 \cdot 10.41\text{H}_2\text{O}$.

Pure Ferro-molybdenums.—Em. Vigouroux.—The author obtains a series of pure ferro-molybdenums, containing about 80 per cent of molybdenum, by the direct union of iron and molybdenum. These ferro-molybdenums contain four bodies corresponding to definite formulæ. Fe_2Mo should constitute the lowest definite compound capable of being produced in synthesised ferro-molybdenums. This can be obtained from an ingot containing 12.5 per cent Mo

and sufficient iron to form Fe_{12}Mo . Hydrochloric acid dissolves away the iron only, without a trace of molybdenum, and the action only ceases when the residue contains 46.2 per cent of molybdenum.

Influence of the Juxtaposition of the Ketonic and Acid Functions in the same Molecule.—L. J. Simon.—The author showed that the action of pyruvic acid on urethane is an equilibrium action comparable with the etherification of an acid by an alcohol:—



The diurethane pyruvic acid, insoluble in water, slowly disappears by decomposition, and, inversely, the evaporation of the water in a vacuum or on a water-bath causes the initial acid to be reformed. The author investigates the reactions when other solvents, such as alcohol, are used.

Condensation of Acetylenic Amides with Phenols. General Method of Synthesis of β -Oxyphenol Ethylenic Amides.—Ch. Moureu and J. Lazennec.—The acetylenic nitriles can be condensed with alcohols and phenols with formation of addition products resulting from the fixation of the alcoholic or phenolic molecules on to the acetylenic liaison. The acetylenic amides, $\text{R—C}\equiv\text{C—CONH}_2$, are susceptible of giving products of analogous condensation. The authors also describe their experiments with phenols which give well-defined bodies; their composition can be exactly determined by an examination of their hydrolysis products. Under the influence of hot 10 per cent sulphuric acid they are completely decomposed at the end of several hours' boiling with reflux condenser into the corresponding acetone and phenol.

MISCELLANEOUS.

Radio-Activity.—Messrs. Archibald Constable and Co. will publish very shortly a new book by Professor Harry C. Jones, of the Johns Hopkins University, entitled "The Electrical Theory of Matter and Radio-Activity." Professor Jones reviews the whole subject, and brings into line the latest results obtained.

The Society of Dyers and Colourists (London Section).—The Second Annual Dinner of the London Section of the Society of Dyers and Colourists will be held at the Criterion Restaurant, Piccadilly Circus, W., on Wednesday, May 23rd, at 7.30 p.m. Those interested in dyeing and the allied industries who are not members of the Society are specially invited. Tickets 5s. each, and particulars may be obtained from members of the committee, or the Hon. Secretary, Wallace Burton, 219, Shooter's Hill Road, Blackheath, S.E.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst., His Grace the Duke of Northumberland, K.G., President, in the chair. Mr. H. Ballantyne, Sir Walter Balfour Barttelot, Bart., Dr. Gustav Hamel, Mr. W. M. Mordey, and Captain Adrian Rose were elected members. The special thanks of the members were returned to Professor J. A. Fleming, F.R.S., for his donation of £26 5s. to the fund for the promotion of Experimental Research at Low Temperatures. It was announced that His Grace the President had nominated the following Vice-Presidents for the ensuing year:—The Right Hon. Lord Alverstone, G.C.M.G., Sir William Huggins, O.M., K.C.B., The Right Hon. Lord Kelvin, O.M., G.C.V.O., Dr. Ludwig Mond, The Right Hon. Lord Sanderson, G.C.B., K.C.M.G., The Right Hon. Sir James Stirling, Sir James Crichton-Brown (Treasurer), and Sir William Crookes (Honorary Secretary).

The International Association for Testing Materials.—It is arranged that this Association, which holds its congresses about every three years in industrial centres in various countries, shall this year meet in the Academy of Science at Brussels, from September 3 to 8. The King of Belgium accords the Congress his patronage, while Prince Albert of Belgium will be one of the honorary presidents, as also will the Ministers of Finance, Railways, War, and Trade, and the Mayor of Brussels. The programme of excursions includes visits to the Harbour Works at Brussels and at Antwerp, the Steel Works of the John Cockerill Company at Seraing, the Arsenal at Mechlin, and the Harbour Works at Zeebrugge. Among the papers to be read will be one on the Industries of Belgium, by Baron E. de Laveleye and M. Camerman. It is expected that a considerable number of members and delegates from this country will be present at the Congress. Mr. J. E. Stead, F.R.S., Middlesbrough, is the English Secretary of this institution.

Institute of Chemistry of Great Britain and Ireland.—*Pass List of the April Examinations.*—Of seven candidates who entered for the intermediate examinations, six passed: C. T. Bennett, B.Sc. (Lond.); S. H. Groenewoud; B. R. James; G. R. W. Lawson; E. H. Merritt, B.Sc. (Lond.); and C. A. Wonham, B.Sc. (Lond.). In the final examination for the Associateship (A.I.C.), of four examined in the branch of Mineral Chemistry, three passed: G. N. Bacon, Assoc. R.C.Sc. (Lond.), B.Sc. (Lond.); F. M. G. Johnson, M.Sc. (Montreal); and E. J. Wilson, B.A. (Cantab.). Of four in the branch of Metallurgical Chemistry, one passed: H. J. Bailey. Two candidates presented themselves in Organic Chemistry, and both passed: L. H. Berry, and O. W. Stickland, B.Sc. (Lond.). Of seven who entered in the branch of the Analysis of Food and Drugs and of Water, including an examination in Therapeutics, Pharmacology, and Microscopy, the following five passed: B. J. Eaton, W. R. Mummary, F. L. Okell, R. P. Page, and R. G. Pelly. The examiners in chemistry were Mr. W. W. Fisher, M.A., F.I.C., and Dr. G. G. Henderson, M.A., F.I.C. The examination in Therapeutics, Pharmacology, and Microscopy was conducted by Dr. F. Gowland Hopkins, M.A., F.R.S., F.I.C.

Society of Dyers and Colourists.—*Prizes for the Solution of Technical Problems:*—

1. Prize of £20 for a full investigation of the average degree of tendering brought about in cotton-yarn of various qualities by—(a) Cross dyeing with acid colours, and (b) dyeing aniline black, with the object of fixing standards for the trade.
2. Prize of £10 for a practical method of so treating or preparing cotton-yarn as to cause it to resist direct dyeing cotton colours. (The object desired is the production of a pattern or mixed effect in the piece dyeing of all cotton goods).
3. Prize of £10 for a practical method of dyeing full shades of basic colours on cotton, fast to rubbing.
4. Prize of £10 for a practical method of causing kemps, when present in yarn or piece goods, to take the dyestuff equally with the accompanying wool.
5. Prize of £20 for a full investigation of the mordanting properties of various tannin materials, more especially—(a) As to the relative affinity for cotton of the tannins of galls, myrabolams, sumach, divi-divi, &c.; (b) as to the relative fastness of the colour lakes produced with these tannins and basic colours, in conjunction with antimony, tin, and iron; (c) as to the best method of determining by volumetric analysis, or other means, their relative mordanting power.
6. Prize of £20 for a cheap and practicable method of producing a good black on Tussur silk.
7. Prize of £50 for a practical method of so treating with some non-deliquescent substance, cotton pieces

goods dyed logwood black and heavily filled, as to render them mildew proof in tropical climates without impairing either colour or finish. Competitors may obtain further details relating to this prize on application to ERNEST T. HOLDSWORTH, Hon. Sec., 10, Merton Road, Bradford.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Estimation of Boron.—Would one of your readers supply a reference where I can find methods of determining boron in alloys with iron and manganese, and also of estimating boric acid by means of standard alkaline solutions? Also, what indicators are applicable for this purpose?—A. A.

MEETINGS FOR THE WEEK.

- MONDAY, 14th.**—Society of Arts, 8. (Cantor Lectures). "Heraldry in relation to the Applied Arts," by George W. Ebe.
- TUESDAY, 15th.**—Royal Institution, 5. "Glands and their Products," by Prof. William Stirling, M.D., &c.
— Faraday Society, 8. "The Electrolysis of Fused Zinc Chloride in Cells Heated Externally," by Julius L. F. Vogel. "Sensitiveness of the Platinum Electrode," by H. D. Law.
- WEDNESDAY, 16th.**—Society of Arts, 8. "The Development of Water-marking in Hand-made and Machine-made Papers," by Clayton Beadle.
— Microscopical, 8. Exhibition of Pond Life.
- THURSDAY, 17th.**—Royal Institution, 5. "The Influence of Ptolemaic Egypt on Græco-Roman Civilisation," by the Rev. J. P. Mahaffy, C.V.O., D.D., &c.
— Chemical, 8.30. "Relation between Absorption Spectra and Chemical Constitution—Part VI., The Phenylhydrazones of Simple Aldehydes and Ketones," by E. C. C. Baly and W. B. Tuck. "Aromatic Compounds obtained from the Hydroaromatic Series—Part II., Action of Phosphorus Pentachloride on Trimethyl-dihydroresorcin," by A. W. Crossley and J. S. Hills. "Studies of Dynamic Isomerism—Part V., Isomeric Sulphonic Derivatives of Camphor," by T. M. Lowry and E. H. Magaon. "Studies on Basic Carbonates—Part I., Magnesium Carbonates," by W. A. Davis.
- FRIDAY, 18th.**—Royal Institution, 9. "International Science," by Prof. Arthur Schuster, F.R.S., &c.
- SATURDAY, 19th.**—Royal Institution, 3. "The Old and the New Chemistry," by Prof. Sir James Dewar, D.Sc., F.R.S., &c.

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DIAMONDS.

A Lecture delivered before the British Association. at Kimberley.

By **SIR WILLIAM CROOKES**,
Hon. D.Sc. (Oxford, Dublin, and Cape of Good Hope), F.R.S.

16, NEWCASTLE ST., FARRINGTON ST., E.C.

THE CHEMICAL NEWS.

VOL. XCIII., No. 2425.

BACK REACTIONS IN IODINE TITRATIONS.

By JOHN HUGHES DAVIES and EDGAR PHILLIP PERMAN.

It is often noticed when making quantitative determinations involving the liberation of iodine from potassium iodide and the titration of the liberated iodine by sodium thiosulphate or arsenious acid solution, using starch as an indicator, that the end-point of the reaction is uncertain owing to the reappearance of the blue colour on standing a short time. We are not aware that any explanation of this phenomenon has been offered, and have now made some experiments in order to throw light on the subject.

We find that the appearance or otherwise of the "back reaction" depends on the concentration of the potassium iodide in solution. The "back reaction" is most marked in those cases in which the iodine is liberated by copper sulphate or potassium dichromate, but takes place only to a very slight extent when bleaching-powder or permanganate is used.

The explanation of the reappearance of the blue colour lies evidently in the comparative slowness (and incompleteness) of the liberation of iodine from potassium iodide, in dilute solution, by the substances mentioned. Sufficient increase of concentration of the iodide solution makes the reaction very nearly instantaneous, and thus increases the accuracy of the titration by avoiding any possible "back reaction." It was found that suitable quantities of potassium iodide were 1 gm. in 10 c.c. water for 25 c.c. $N/10$ $K_2Cr_2O_7$ solution, and 2 grms. in 20 c.c. water for 1 gm. $CuSO_4 \cdot 5H_2O$ in 50 c.c. water.

University College, Cardiff.

NOTE ON THE SAMPLING OF GOLD ALLOYS.

By ERNEST A. SMITH, A.R.S.M.

IN assaying the various gold alloys used by jewellers and goldsmiths, great care has to be exercised in the selection of the sample, as the surface is usually richer in gold than the interior, in consequence of the pickling or blanching to which these alloys, whether in the form of sheet metal, wire, or gold wares, are invariably subjected.

During the process of manufacture the alloys, which consist of gold alloyed with copper and silver in various proportions, require to be repeatedly heated to a red-heat for annealing and for soldering purposes, with the result that the copper of the surface is oxidised more or less deeply.

To remove the coating of oxide thus formed the alloys are dipped for a short time in hot dilute sulphuric acid or nitric acid, which dissolves the copper oxide and leaves a film of more or less pure gold.

It is evident that these operations, repeated several times on the same piece, produce a refining of the surface, the fineness of which is notably different from the rest of the mass. Consequently, one of the first precautions to be taken when sampling these alloys for assaying is to remove this enriched or coloured surface, as it is obvious that if it is included in the sample the result obtained will not represent the true fineness of the alloy but will be above it. The thickness of the film of gold resulting from the pickling necessarily varies considerably, and is chiefly dependent on the composition of the alloy, the strength and nature of the acid used, and the length of time the alloy is allowed to remain in the acid.

It may be pointed out that finished articles of jewellery and of goldsmiths' work are very frequently coloured by a

special process, the film of gold in this case being usually thicker than that which results from the ordinary pickling process; but gold articles when submitted for assay are invariably in an unfinished condition, and have only been subjected to immersion in dilute acid to clean them.

No figures appear to have been published hitherto to show to what extent the accuracy of the gold assay may be affected by including the coloured surface in the assay sample; the following results therefore, based on several years' experience with these alloys, may not be without interest.

The gold alloys received from bullion dealers are usually in the form of thin sheet or wire, and can, as a general rule, be readily sampled by cutting off a piece with the shears or pliers; but in the case of gold wares and jewellery, owing to the nature of the articles, it is very seldom that a cutting sample can be obtained without risk of injuring the article, and careful scraping of the surface has to be resorted to. A scraping sample, however, is not so satisfactory, and it is advisable to take a cutting sample whenever possible, as it will more truly represent the mass of the metal than a sample scraped from the surface.

It is hardly necessary to say that when the coloured surface is included in the sample the errors in the gold assay are much greater with a scraping sample than with a cutting sample, as the former will contain a larger proportion of the enriched surface.

Experience has shown that, under similar conditions of pickling, the errors are usually greater with alloys in which the gold is alloyed mainly or entirely with copper than with alloys in which the copper is partly or entirely replaced by silver, as the copper is more readily acted upon by the acid during pickling.

The figures given in Table I. show to what extent the results of the gold assay are influenced by the coloured surface in the case of samples cut from sheet metal. Samples of sheet metal of different gold standards were carefully cleaned and rolled to various gauges, then simultaneously heated to a dull red heat, and pickled in hot dilute nitric acid for two minutes to ensure uniformity of treatment.

When removed from the acid the strips were rinsed in distilled water and dried. To ascertain the true fineness of the alloys, separate assays were made on samples from which the coloured surface had been carefully removed.

The assays were made in the ordinary way, check assays being added in all cases.

TABLE I.—Assays of Cutting Samples, including Coloured Surface.

	Thickness of sheet				
	B.M.G.	Inches.	Description of sample	Gold per 1000 parts.	Difference per 1000 parts.
<i>Sample A, 9 Carat Gold Sheet.</i>					
1.	11	0.032	Colour removed	375.0	—
2.	11	0.032	Colour included	380.6	+5.6
3.	8	0.021	" "	380.8	+5.8
4.	4	0.012	" "	381.3	+6.3
5.	1	0.008	" "	381.5	+6.5
<i>Sample B, 9 Carat Gold Sheet.</i>					
1.	8	0.021	Colour removed	376.6	—
2.	8	0.021	Colour included	382.0	+5.4
3.	4	0.012	" "	384.6	+8.0
4.	1	0.008	" "	389.3	+12.7
<i>12 Carat Gold Sheet.</i>					
1.	8	0.021	Colour removed	500.1	—
2.	8	0.021	Colour included	500.3	+0.2
3.	4	0.012	" "	500.4	+0.3
4.	1	0.008	" "	500.8	+0.7
<i>15 Carat Gold Sheet.</i>					
1.	8	0.021	Colour removed	631.2	—
2.	8	0.021	Colour included	632.0	+0.8
3.	4	0.012	" "	632.1	+0.9
4.	1	0.008	" "	632.5	+1.3

As previously stated, the duration of the pickling has an important bearing on the assay result, and with commercial samples it is not an uncommon thing to get greater differences than those given in the table, when the colour is not removed.

As a general rule, the errors are smaller with the alloys of higher standard, as there is less base metal to be dissolved out.

With samples cut from the sheet the thickness of the metal necessarily plays an important part, the errors resulting from the coloured surface being minimised with an increase in the thickness of the sheet. Metal sheet gauged to the higher gauges given in the table is that most frequently met with in goldsmiths' work, but metal rolled to the lower gauges is also in use.

In the year 1900, it was decided by the wardens of the various assay offices that "in future no hollow gold wares would be assayed and hall-marked if made of a thinner gauge than No. 36 of the legal standard wire gauge, the equivalent of which is 0.0076 inch" (*Thirty-third Mint Report*, 1902, p. 67), or slightly thinner than No. 1. of the Birmingham Metal Gauge, by which sheet metal is invariably gauged.

It may be pointed out, however, that the decision applies only to *hollow* gold wares, and as the authorities at the assay offices have no jurisdiction over the manufacture of jewellery it not infrequently happens that articles made from very thin sheet are submitted for assay.

The errors introduced by including the coloured surface in a scraping sample are given in Table II.

The first sample in each case was obtained by carefully scraping the surface until the natural colour of the alloy was reached; the second sample was then scraped from the same place.

As the first scraping removes not only the outer layer but more or less of the original alloy, it necessarily follows that the assay results will vary in accordance with the depth to which the scraping has been carried. In the case of articles made from very thin sheet, a large surface has to be scraped in order to secure a quantity sufficient for assay, and as the sample under these conditions will consist very largely of the coloured surface, the errors on the gold assay are necessarily very considerable.

This fact accounts for some of the very high results given in the table.

A larger number of results have been given for 9 carat gold than for any other standard, this alloy being the one most frequently received for assay, more than 50 per cent of the wares passing through the Government Assay Offices for hall-marking being made from gold of this standard.

TABLE II.—Assays of Scraping Samples, including Coloured Surface.

Sample.	Gold per 1000 parts.		Difference due to coloured surface. Per 1000 parts.
	First scraping (including colour).	Second scraping (correct fineness of alloy).	
9 Carat Gold.			
A.	392.8	382.0	+10.8
B.	489.0	392.0	+97.0
C.	424.0	376.3	+47.7
D.	514.5	378.8	+135.7
E.	440.0	382.0	+58.0
15 Carat Gold.			
A.	706.8	630.2	+76.6
B.	703.5	630.0	+73.5
C.	688.7	632.4	+56.3
18 Carat Gold.			
A.	772.6	755.7	+16.9

In taking scraping samples, after removing the coloured surface, it is very important to scrape as deeply as the nature of the article will permit, especially with articles which have been subjected to any stamping operations in

the course of manufacture; this will be evident from the following example, which is by no means an isolated case.

Three scraping samples were taken from a sheet of 15 carat gold of about 18 B.M.G. which had been repeatedly struck between steel dies, and assayed for gold with the following results:—

	Gold per 1000 parts.
First scraping (including coloured surface) ..	633.0
Second scraping	623.7
Third scraping	625.0

As the second assay gave a result a little below the legal 15 carat standard, viz., 625.0 per 1000, the third scraping sample was taken and assayed with the result quoted. From these results it would appear that the oxide resulting from the several annealings was only removed by pickling after the final annealing and not after each annealing, with the result that the oxide was driven into the metal when it was stamped between the dies, giving rise to the low result of the second sample. To confirm the result of the third scraping sample, a piece of metal was cut from the sheet, and the coloured surface removed. When assayed it was found to be 625.0 fine, thus proving that the third scraping sample truly represented the bulk of the alloy.

The results given in the tables prove the impossibility of getting a correct result for the gold content of an alloy when the external layer is introduced into the sample, whether taken by cutting or by scraping, and they also emphasize the importance of carefully removing the coloured surface from gold alloys of all standards before taking the sample for assay, particularly when scraping samples have to be taken.

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

PART II.—ANALYSIS OF THE TUNGSTEN GROUP.

By ARTHUR A. NOYES.

(Continued from p. 218).

Test Analyses (continued).

Tantalum.—This element was present in quantity of 2 m.grms. in fourteen of the mixtures analysed, of 3 m.grms. in two of them, and of 1 m.grm. in one of them. A satisfactory test for it was obtained in every case, except one (T. A. 3) in which 300 m.grms. of titanium and 300 m.grms. of tin were simultaneously present, and it was found, even in this mixture, in a second analysis (T. A. 5). Its detection succeeded repeatedly in the presence of 300 m.grms. of titanium, or in that of 300 m.grms. tungsten, or in that of 300 m.grms. tin. It succeeded also in the cases where 400–500 m.grms. molybdenum (T. A. 16, 37), or 100 m.grms. niobium (T. A. 15), or 400 m.grms. antimony (T. A. 36) were present. Two m.grms. can therefore always be detected.

The "blank" tests for tantalum (that is, those in the absence of this element) were somewhat inconclusive in those mixtures containing much titanium (T. A. 9, 11, 32, 35), owing to the presence of a minute quantity of tantalum in the titanium sample used; but the precipitates were always very small (1–2 m.grms.), and there is little doubt that with pure material perfect blanks would be obtained. In two cases (T. A. 31, 32), also, a light flocculent precipitate separated in place of the heavy viscous one characteristic of tantalum. Good blanks were obtained in the other cases (T. A. 2, 28, 34, 38). While a further study of the blanks obtaining in testing for this element according to the procedure is desirable, especially since no good confirmatory test for it is known, yet it is hardly possible that error will be made, even with respect to small quantities, by any one who first makes himself familiar

* From the *Technology Quarterly*, xvii., No. 3.

with the appearance of the potassium fluoxytantalate and fluotitanite.

Niobium.—There would be no difficulty whatever in detecting 2 m.grms., or even less, of this element, provided the first test with mercuric chloride could be relied upon; but owing to the possible presence of tungsten or molybdenum, it is ordinarily necessary to fuse with sodium carbonate and sulphur, and then apply a second test. The results show that under these circumstances 2 m.grms. is near the limit of detection. This quantity was present in nine of the mixtures analysed; and the second test failed in five, and succeeded in three of them (it being omitted in one case). Three m.grms. were present in two mixtures and 5 m.grms. in two others, and in all of these the test was satisfactory. It succeeded with 2 m.grms. in the presence of 400 m.grms. of antimony (T. A. 31), or of 200 m.grms. of titanium (T. A. 12), or of 100 m.grms. tantalum (T. A. 14), and with 5 m.grms. in the presence of 300 m.grms. of tin (T. A. 11, 19). It seems safe to conclude that 3 m.grms. can be detected under almost any conditions.

The question of blank tests for this element in the presence of much titanium, tungsten, or molybdenum is an especially important one, and many mixtures were prepared and analysed with reference to it. A perfectly clear solution, or a slighter turbidity than would have resulted from 1 m.grm. of niobium, was obtained in the second mercuric chloride test from nine mixtures containing 300—500 m.grms. of titanium. In three of these mixtures 300—400 m.grms., and in two of them 4—5 m.grms. tungsten were simultaneously present. The result, too, was satisfactory in the four cases where tungsten was present with only a small quantity of titanium. This was also true where the mixtures contained much tin, either with or without much tungsten. In two of the five mixtures (T. A. 16, 35) in which 300—500 m.grms. of molybdenum were present, the second mercuric chloride test showed a decided turbidity, while in the other three (T. A. 17, 31, 39) a good blank was obtained; but in all these analyses except the last (T. A. 39) the ammonium sulphide precipitate was not re-digested with ammonia—a precaution that was adopted only near the end of the work. The results of the blank tests for niobium may therefore be considered satisfactory under all circumstances, provided regard is paid to all the precautions described in the procedure.

Titanium.—The results for this element require little discussion. The yellow or orange-red colour produced with hydrogen peroxide constitutes so delicate a test that in every mixture containing 1 or 2 m.grms. of it, it was conclusively detected. The test is so characteristic that blank tests were considered unnecessary, especially since its presence is ordinarily confirmed by the reddish violet colour produced with zinc.

Tin.—The only analyses in which the final procedure for the separation and detection of tin was employed are those of the third and fourth series; but Test Analyses, 1, 2, and 8 also deserve consideration, since the omission of the ignition of the sulphide could hardly affect the tin test. The results show that 2 m.grms. escape detection when 400 m.grms. of either titanium (T. A. 32), antimony (T. A. 31), or molybdenum (T. A. 34) are present, and that this is true of even 4 m.grms. in the presence of 400 m.grms. of molybdenum (T. A. 37), or in the simultaneous presence of 400 m.grms. of titanium and an equal quantity of molybdenum (T. A. 35) or tungsten (T. A. 33). On the other hand, the test succeeded with 4 m.grms. of tin in presence of 400 m.grms. of antimony (T. A. 36), with 8 m.grms. of tin in the presence of 400 m.grms. of molybdenum (T. A. 44), and with 1 m.grm. of tin in the presence of 300 m.grms. of tungsten (T. A. 42), or of 100 m.grms. of titanium (T. A. 2). It seems therefore fair to set the limit of detection at 3 m.grms. in the presence of much antimony or titanium, at 6 m.grms. in that of much molybdenum, and at 1 m.grm. in that of much tungsten.

Blank analyses were considered unnecessary, since experiments (see C. E., P. 41, N. 1) showed the complete

insolubility in hot hydrochloric acid of the ignited sulphides of the other elements which reduce mercuric chloride.

Tungsten.—In the case of this element, all analyses except those of the first series were made by the final procedure. The analyses of the first series in which the test succeeded (T. A. 2, 7, 22, 23) also deserve consideration, since the omission in them of the ignition of the sulphide could only have the effect of making the test less delicate. It will be seen from the tables that the detection of 2 m.grms. failed in the presence of 300—400 m.grms. of antimony (T. A. 31), or of titanium (T. A. 29), or of 100 m.grms. or more of molybdenum (T. A. 28, 31, 47); and that that of 4 m.grms. failed in the simultaneous presence of 400 m.grms. each of titanium and molybdenum (T. A. 35). On the other hand, 3 m.grms. were detected when no other element was in great excess (T. A. 2, 27) or when much tin was present (T. A. 40, 41); and 4 m.grms. were detected when the mixture also contained 400 m.grms. of titanium (T. A. 32) or of antimony (T. A. 36), or 100 or more m.grms. of molybdenum (T. A. 34, 37, 46). Eight m.grms. were detected in the presence of 20 m.grms. of phosphate (T. A. 43), but a less quantity could probably have been found. The limit of detection may therefore be set at 2 m.grms. when it is present either alone or with a large quantity of tin, and at 3 or 4 m.grms. when a large quantity of antimony, titanium, or molybdenum is simultaneously present.

Molybdenum and tin are the only elements that could give rise to a precipitate in a blank analysis at the point where the ignited sulphides are dissolved in nitric and hydrochloric acid (P. 43); and mistake from this source is entirely guarded against by the subsequent evaporation with sulphuric acid, and by the confirmatory test with zinc.

Antimony, Arsenic, and Molybdenum.—The final detection of these elements is effected in connection with the later groups. It is therefore sufficient to show that even a small quantity of any of them present in the solution of this group is precipitated by hydrogen sulphide from the hydrofluoric acid solution (P. 31). This is shown by the above analyses for 1 or 2 m.grms. of antimony (T. A. 1, 25, 26) and of molybdenum (T. A. 1, 32, 33). Special experiments have confirmed this result, and have shown that 2 m.grms. of arsenic are also precipitated (see C. E., P. 31, N. 3).

Summary.—The preceding discussion may be summarised by the following statements:—Four m.grms. of any element of this group, when present in the hydrofluoric acid solution at the start, can be detected with certainty by the procedure described in this article, even when a quantity as large as 300—400 m.grms. of any other element of the group is simultaneously present. Two m.grms. of titanium, tantalum, antimony, arsenic, or molybdenum, or three of niobium, can be detected with certainty in any combination whatever with other elements. Two m.grms. of tin or tungsten can each be detected alone or in the presence of a very large quantity of the other, but not in the presence of a large quantity of the elements precipitated by hydrogen sulphide or ammonium sulphide. Eight m.grms. of tungsten, and probably much less, can be detected in the presence of a considerable quantity of phosphate. There is no possibility of concluding that any absent element is present as a result of a failure of the final test to yield a blank, except in the cases of tantalum and niobium; and observance of all the precautions described and of the remarks as to the interpretation of the results will prevent any mistake in these cases.

In conclusion, it need hardly be said that skill in the manipulation of exact qualitative analysis and some slight experience with this process itself are essential in order to secure the degree of delicacy just referred to it. But the attempt has been made to make the directions so detailed and explicit that it is believed that an analyst possessing such skill will be able to approximate closely to these results after working through a single mixture containing small quantities of all the elements of the group.

(To be continued.)

AN IMPROVED EXTRACTION CUP.

By E. BRUCE WARREN.

THIS cup has been designed for general extraction purposes, the novel feature being that the substance under treatment whilst being acted upon by the pure solvent is kept at the

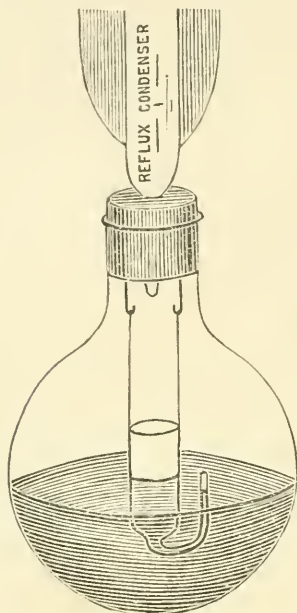


FIG. 1.

temperature of the boiling-point of the solvent employed, thus greatly facilitating the extraction of difficultly soluble substances. Figs. 1 and 2 show two designs of this cup.



FIG. 2.

In Fig. 1 the cup has a discharging pipe from the bottom, which is carried upwards to a point below the top

of the cup. This form of cup enables the residue to be dried in a stream of any gas if the substance is likely to undergo any change during drying in the ordinary way.

In Fig. 2 the cup containing the substance under examination is supported in a tube, and the solvent is kept in the cup at a height corresponding to the height of the outer tube.

In use, the bottom of the cup is covered by a plug of wool or other suitable substance and the material under examination is weighed into it. The cup is placed in a flask, sufficient solvent poured in, and the flask fitted with a reflux condenser arranged to let the condensed solvent fall back into the cup. This percolates through the material and passes away with the soluble matter through the outlet back into the flask. After the extraction is completed, the residue can be dried in a current of gas by connecting up with the outlet of the cup.

We have found this design of extraction apparatus to yield very satisfactory results at the Indiarubber Works at Silvertown, being both efficient and rapid; substances even as difficultly soluble as Carnaüba wax being extracted by acetone in a short time.

This cup is manufactured by Messrs. Müller, Orme, and Co., and is sold by them under the name of the "Flow."

A REVISION OF THE ATOMIC WEIGHTS OF
SODIUM AND CHLORINE.*

By THEODORE WILLIAM RICHARDS

and
ROGER CLARK WELLS.

(Continued from p. 219).

THE RATIO OF SODIC TO ARGENTIC CHLORIDE.

Two obvious means are available for determining the combining weight of sodic chloride—one, by weighing the amount of argentic chloride which may be made from a given weight of this salt; the other, by discovering the weight of silver needed to precipitate all its chlorine. Both these methods involve a consideration of all the special points mentioned in the preceding sections, and both are essentially gravimetric, although both involve the use of the nephelometer in order to estimate the last traces of silver or chlorine in the supernatant liquid.

The actual investigation of these two methods proceeded simultaneously in order to economise the time during the long delays to which each was frequently subject. Indeed, in some of the previous work in this laboratory, where the pure materials were scarce, the two methods were actually combined in the same analysis, by first determining the weight of silver needed to precipitate the chloride, and then weighing the chloride produced. This last procedure is, nevertheless, somewhat objectionable on account of its complication. It is, moreover, subject to slight opposing errors; the avoidance of one of these involves the admission of the other, as has already been pointed out in a preceding communication (Richards and Archibald on the Atomic Weight of Cæsium, *Proc. Amer. Acad.*, 1903, xxxviii., 443). The magnitude of the uncertainty thus caused is not great, and the final error involved is insignificant even in atomic weight investigation of ordinary calibre, usually not exceeding 0.01 per cent; but in the present case extraordinary accuracy was sought. Hence, although the methods were studied simultaneously, they were never combined in the same analysis. For this reason the work is easily divided into two sections, each treating one of the two ratios named above. Of these it is convenient to discuss first the ratio of the chlorides to one another; and this discussion is taken up in the present chapter.

After the preliminary experiments had indicated the nature of the problems involved, a single specimen of pure

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sodic chloride was used for analysis until all the details of analysis were perfected. Then the various samples of salt were analysed by methods of known precision. The temptation to vary two conditions in a single new experiment is thus easily avoided. The detailed description of every step of the analytical process follows.

It was soon found that salt, when free from excess of acid, can be fused in a platinum crucible in the air without either attacking the crucible to an important extent, or becoming appreciably alkaline. Quantitatively, it was later proved, as will be shown, that salt thus prepared is identical to that fused in a platinum boat in a vacuum and transferred and weighed in the familiar "bottling apparatus" which has served so conveniently for hygroscopic substances. It was found, moreover, that a crucible full of salt thus prepared did not gain in weight during the operation of weighing, on account of the dry winter atmosphere of the steam-heated weighing-room. Probably this would not have been the case in a warm climate; but being the case, it facilitated greatly the present work.

The crucible generally used for fusing the salt was, of course, previously freed from iron, and during twenty-three fusions it lost only 0.47 m.grm., or 0.02 m.grm. each time. It is possible that a portion of the weight was lost by volatilisation during the preliminary ignitions of the crucible when it was being prepared for weighing alone; but probably most of this trace of platinum went into solution in the salt. The weight of the crucible before fusion was always taken as the true one, however; therefore even this slight possibility of loss of course could not affect appreciably the quantitative result.

During the fusion of the salt the crucible was enclosed in a larger covered Berlin porcelain crucible, especially made to fit it, and heated by a blast-lamp in a small clay furnace. The products of combustion were suitably deflected, so that only pure air should be in contact with the salt in the crucible. The fused salt was cooled in a desiccator in the balance room, and the weighing was conducted by the substitution of a suitable tare-crucible, as usual.

In order to avoid all risk of accidental loss, the salt was dissolved from the crucible by placing it in a large covered beaker, and after covering it carefully with water, agitating it gently from time to time until solution was complete. This solution, thus carefully prepared, was transferred to a 2-litre Erlenmeyer flask with a well-ground glass stopper, where it was diluted to suitable volume (over 5 litres per mol.). Here it was precipitated by the at least equally dilute argentic nitrate in excess. The precipitate was freed from the supernatant mother-liquor by filtration as soon as it had cleared enough to make this separation possible. Promptness is needed in order to avoid the permanent occlusion of sodic and argentic nitrate in the manner already stated, but too great promptness prevents complete precipitation of the silver halide. About fifteen hours are usually allowed for the settling of the solution. Agitation is not necessary.

The clear supernatant liquid was decanted through a large carefully prepared Gooch crucible. The mat of this Gooch filter, through which all the mother-liquor and wash-waters were passed, was prepared of selected fibrous asbestos shreds, which had been boiled with nitric acid and well washed. The mat was a trifle thicker than a filter-paper—so that the holes of the crucible were indistinctly visible when viewed in front of a strong light—and was not allowed to extend up the sides of the crucible. A preliminary ignition of the mat was found to result in a slight disintegration and brown coloration, and caused loss during washing; therefore before weighing the mat was dried at a lower temperature, namely, about 150°. This same temperature was used later in drying the argentic chloride. During the operation of washing, at first all but a trace of the precipitate was left in the flask, and it was then re-washed by decantation. After each washing, the precipitate was allowed to drain several minutes, for silver chloride is known to hold water like a sponge. At the

second or third washing a disintegration of the precipitate often took place, resulting in an emulsion-like mixture, but in most cases this could be prevented by the presence of a little nitric acid. The precipitation had been made with silver nitrate in excess. The first three washings, of 0.2 litre each, were made with very dilute silver nitrate, and this was displaced in the fourth washing by about 0.05 litre of pure water. In such wash waters, which, with the mother-liquor, usually amounted to about 2 litres, no trace of chloride could be found by the nephelometer. The main weight of silver chloride was corrected by + 0.06 m.grm., however, in every case, for the otherwise determined solubility in such wash waters (see p. 203). From five to eight subsequent treatments with pure water, very slightly acid, in 0.1 litre portions, completed the washing. These later wash waters were treated in the manner described below, in order to determine the chloride which they always contained.

The precipitate was now transferred to the filtering crucible wholly by means of a stream of water. It was found convenient first to transfer and pack down by air pressure a small portion of the precipitate on the asbestos mat, in order that the greater part of the argentic chloride might be easily separated from this mat for fusion. By resting the lip of the flask on the Gooch crucible it is possible to direct a stream of water from a wash-bottle into the flask and finally wash out every particle of precipitate. In the most careful experiments the wash-bottle was provided with protecting bulbs to preserve the purity of the water, or was dispensed with altogether, being replaced by a jet driven by hydrostatic pressure. At this stage the cloth covering was necessarily removed from the flask. The flask was finally rinsed with ammonia, which was carefully tested for a possible trace of silver chloride.

On drying the precipitate the temperature was made to rise very slowly above 100° during two or three hours. This deliberate drying was found to be more effective than the immediate application of high temperature, presumably because a hard coating was not then formed about the mass of the precipitate. Finally, the temperature was maintained at about 150° for two or three hours longer. In this way fairly constant weight is easily attained, which fifteen hours' further heating at 150° changes very slightly. The last traces of water were always expelled by fusion, as is described below.

In many of the experiments the silver chloride was dried in an electric drying oven heated by hot platinum wires conveying a current of an ampère or two (Richards, *Am. Chem. Journ.*, 1899, xxii., 45). When properly constructed this oven gives very satisfactory results. The working of the oven is somewhat more satisfactory if the platinum wires are not heated to redness. In some of the later experiments the precipitate was dried in a clean copper oven heated by a gas flame with no apparent difference in result.

The precipitate thus collected and dried was carefully weighed and then freed from adhering asbestos and transferred to a weighed porcelain or quartz crucible for fusion. The crucible and contents were tared against a similar crucible and contents, and the argentic chloride under examination was then fused in a clean oven constructed from a large porcelain crucible, from the interior of which the products of combustion of the gas were carefully deflected. The fusion is necessary, because minute drops of water are always held by the hardened argentic chloride in sealed cells. It is true that the loss on fusion is not great, never amounting to 0.01 per cent of the weight of the precipitate, but it was enough to receive consideration. In every case it was determined and the appropriate individual correction applied to each weight. The maximum value of the correction was 0.008 per cent, and the minimum 0.003 per cent. That the loss was not due to volatilisation of silver chloride is easily shown by the invariability of the weight upon fusing a second time. That it was not due to accidental reduction was shown in the later experiments by fusing again in a stream of chlorine, when the mass gained on the average only 0.001 per cent. The fused

argentic chloride, even before its treatment with chlorine, was usually pearly and colourless.

In any case, it is clear that this loss on fusion, which has been rejected as of doubtful significance by some authors (Scott, *Journ. Chem. Soc. Trans.*, 1901, lxxix., 147), really represents included water, and must be heeded.

The determination of the weight of the main mass of the precipitate having been thus determined, attention must be directed to several other precautions necessary to ensure exact work. In the first place, all the liquid which has passed through the Gooch crucible was passed through a small washed filter, in order to collect the minute asbestos shreds which even the best fibrous asbestos seems to lose under pressure. This was done as soon as possible after filtration, and before proceeding to solubility determination. A syphon filtering arrangement, or a large inverted flask fitted with a carefully cleansed rubber stopper with two tubes arranged so as to maintain constant level, obviated the tedious process of filtering by hand. The little filter was finally washed free from salts, and the weight of the ignited residue (minus the filter ash) added to the weight of Gooch crucible and precipitate. This residue usually amounted to only one or two tenths of a m.gm. Observation in the microscope easily showed that the residue was really asbestos.

Because it was the object of the research to test every step of the processes involved, the loss and recovery of asbestos shreds was tested by special blank experiments. Large volumes of water were passed through empty Gooch crucibles provided with the usual mats; and the loss of each crucible after drying was found, as well as the weight of shreds recovered from the filtered water. Below are given the results of these blank experiments:—

	Loss of crucible.	Asbestos found.
1	0.00034	0.00034
2	0.00016	0.00045
3	0.00019	0.00016
Average ..	0.00023	0.00032

In two of these experiments the loss very nearly equalled the amount of asbestos found; the other one must have been contaminated by an accidental outside impurity; but the results of the blank experiments are enough to show that the correction is a real one and not to be omitted.

(To be continued).

Royal Institution.—On Thursday next, May 24, at 5 o'clock, Professor W. J. Sollas begins a course of three lectures at the Royal Institution on "Man and the Glacial Period." The Friday Evening Discourse on May 25 will be delivered by Mr. Leonard Hill on "Compressed Air and its Physiological Effects."

Madame Curie.—We quote the following paragraph from *The Times* of May 14th:—"The Governing Board of the Paris University have decided to maintain the Chair of General Physics held at the time of his death by M. Curie, and to propose the name of his widow as their late colleague's successor. The Minister of Education has signed a decree accepting this proposal. M^{me}. Curie was the constant collaborator with her husband in the researches which have made their name famous throughout the world. One of the chief promoters of this movement has been the eminent chemist M. Berthelot."

New Apparatus.—Messrs. John J. Griffin and Sons, Ltd., have recently placed upon the market a novel form of pipette, called the "Struthers Syphon Pipette." It is claimed that it is easier to fill than the old straight form, shorter and more compact, and that the adjustment and flow of discharge can be regulated with great care and precision; it also avoids danger when using corrosive liquids, as there is no need to adjust the liquid to the mark by suction. The same firm have also listed the "Dougal Assay Tube," specially designed to replace the assay flask in parting and similar operations.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

CONVERSAZIONE AT BURLINGTON HOUSE.

ON May 9th the first of the Annual Conversazioni of the Royal Society took place. Among the more important exhibits we note the following:—

Sir OLIVER LODGE, F.R.S., and Dr. ALEXANDER MUIRHEAD, F.R.S. Wireless Telegraphy Apparatus for Military field purposes.

1. A portable pack-transport set of wireless telegraphy apparatus for military field purposes, available for communications across country for distances up to 50 miles, or 150 miles over sea; with electric valves employed to accumulate the impulses of a small coil and battery, or small dynamo, so as to give discharges of energy only otherwise obtainable from a large and heavy source of electric supply. The arrangement needs no earth connection, nor must it have any when it is required to work over long distances with the greatest efficiency.

2. A vibrating needle point-oil-mercury coherer with telephone receiver.

Mr. R. KERR, F.R.A.S. A Torsion Spring for transference of Energy (exhibited on behalf of Prof. L. R. Wilberforce, of University College, Liverpool).

A spring is rigidly fixed to an unyielding support, and, depending, carries a weight of the same diameter, which is adjusted by bolts in such a manner that when the two principal periods of vibration are as nearly equal as possible the transference of energy from an up-and-down motion to a horizontal twisting motion is complete. One pull of the spring is sufficient to cause these motions to be repeated for twenty minutes.

Messrs. WALLACH BROS. Oxygen Rescue Apparatus and other appliances.

1. The "Evertrusty" oxygen apparatus, used by the rescue parties at Courrières, consisting of two oxygen cylinders filled with oxygen, two regenerators through which the vitiated air passes and is regenerated, and which at the same time serve the purpose of ascertaining if the apparatus is in working order prior to use. The fittings and pipes include the mouthpiece, by means of which the air supply is conducted to the mouth of the operator.

2. "Evertrusty" oxygen first aid case for use in case of carbonic oxide poisoning, or after inhalation of smoke, poisonous fumes, &c., consisting of oxygen cylinder, reducing valve, pressure gauge, bag and mask, with back pressure valve.

These appliances permit of active work in atmospheres charged with gas, such as water gas, Dowson gas, Mond gas, power gas, producer gas, blast-furnace gas, after-damp, &c.

Mr. KENNETH J. TARRANT, F.R.A.S. Photographs of Electrical Discharges, at Atmospheric Pressure and *in vacuo*.

A series of photographs showing the characteristic discharge from an interrupted continuous current and a high frequency oscillating one, also between parallel conductors both insulated and bare, of varying capacity, and with various condenser conditions. Also the apparently spiral (vortex) nature of the discharge both in air and *in vacuo*.

Mr. EDWIN EDSER and Mr. EDGAR SENIER. Specimens of Colour Photographs, and Photomicrographs.

1. Lippmann spectrum photographed bleached after Neuhauss's method. The colours seen by reflected light are very bright, and the complementary colours are seen by transmitted light.

2. Colour photograph produced by exposing Lippmann film successively to two continuous spectrums, the red end of one being superposed on the blue end of the other. Two short spectrums are seen on development, crossed by fine dark lines, first observed by Neuhauss.

3. Lippmann spectrum photographs viewed, at polarising angle, through Nicol's prism. Beautiful colour changes occur as the Nicol is rotated.

4. Three-colour photographs of coloured objects, including crystals under polarised light.

5. Photo-micrographs obtained through red, green, and blue colour screens. The blue colour screen improves the resolution very noticeably.

6. Photo-micrographs obtained by the aid of Zeiss apochromatic objective, and other objectives.

7. Simple form of colour sensitometer.

Mr. C. V. BOYS, F.R.S. A Gas Calorimeter.

This calorimeter is of the Hartley or Junkers type; that is, a steady stream of water is passed through the instrument, and the rise of temperature and the rate of flow are measured. The hot gaseous products from a pair of small luminous flames pass up through a short wide chimney which is only water cooled at its base. After impinging upon a bell they pass down and up again in a space in which a motor-car radiator pipe of Clarkson's or other construction is wound. The lower coils are immersed in the water-bath which prevents the chimney from burning, but which does not keep it cool enough to cause condensation within. The water leaves through an equalising chamber above the bell. This is the instrument by which London gas is officially tested.

Sir JAMES DEWAR, F.R.S. Metallic Jacketed Vacuum Vessels.

In these metallic vessels filled with liquid air the vacuum is produced by the use of cooled charcoal. The envelopes may be made of brass, copper, nickel, or tinned iron, with necks made of a bad conducting alloy. The necks can be covered with silvered glass vacuum cylinders which act as stoppers, and at the same time utilise the cold of the slowly evaporating liquid. The efficiency of the best metallic flasks is equal to that of the average silvered glass vacuum vessels now generally used in low temperature investigations. Vessels of this type may be used in industrial cryogenic operations, and for the storage and safe transit of liquid air and oxygen.

Mr. J. E. STEAD, F.R.S. A Triple Alloy of Tin—Antimony—Arsenic, polished and etched, showing bright curved crystals embedded in a soft matrix or eutectic.

A triple alloy containing 75 per cent tin, 20 per cent antimony, and 5 per cent arsenic. After melting and slow cooling it first yields crystals, which assume the form of semi-spherical shells, and a fusible mother substance, the last to solidify, in which, when the alloy is cold, the crystals remain embedded. The crystals contain more arsenic and antimony than the matrix; they are hard and brittle, and capable of taking a high polish. They are not easily corroded by dilute acids, and not readily tarnished. The matrix, or mother substance, containing a preponderating proportion of tin, is easily dissolved out by hydrochloric acid, leaving the curved crystals in bold relief. The specimens exhibited show the fracture and macro-structure of the polished and etched alloy, treated in such a way as to reveal the structure to the best advantage.

Mr. W. ROSENHAIN. Improved Metallurgical Microscope.

Designed for the examination of metal specimens. The base and limb are of particularly rigid construction, and the tube is rigidly attached to the limb. The stage racks on the broad flange of the limb, and is provided with a fine adjustment placed in the line of the optic axis of the microscope. The internal reflectors employed for obtaining "vertical" illumination, instead of being carried on a detachable fitting, are inserted into the tube of the instrument, and are provided with adjusting movements which allow of complete control of the lighting. Various forms of reflectors are readily interchanged without disturbing the focus of the objective. Special devices for the easy attachment and adjustment of oblique and other illuminators for low-power work are provided, while a detachable

bridge can be fitted to the stage so as to adapt it for work with transmitted light. For purposes of photo-micrography a focussing motion is provided whereby the eye-piece may be moved relatively to the objective. Metallurgical specimens are shown illustrating the effect upon resolving power produced by various forms of "vertical" illuminator, and the importance of a concentric rotating stage in this connection.

The Rt. Hon. Lord BLYTHSWOOD. Photographs of certain Arc Spectra.

The spectra were produced by means of a Blythswood concave diffraction grating, the work being undertaken as a practical test of the gratings. The radius of the grating was ten feet, the first order spectrum being photographed. The total length given is about forty inches, from λ 2100 to λ 7400. There was no screening for the violet end. The red end was taken on films dyed with pinacyanol, a screen placed in front of the slit completely eliminating the second order spectrum. Salts of the elements were fed into a carbon arc on a 100 volt circuit. The photographs were taken by Mr. Walter A. Scoble, B.Sc.

Dr. O. SILBERRAD and Mr. H. A. PHILLIPS. A Series of Picrates.

The salts of picric acid are of interest as having been the probable cause of some of the most disastrous lyddite explosions on record. The specimens exhibited were in many cases prepared in the course of an exhaustive investigation recently carried out at the Research Laboratories of the Royal Arsenal. Several of the salts exhibited have never been prepared before, and the majority have never previously been obtained pure or correctly analysed. For example, nickel picrate, according to previous investigations, is capable of forming hydrated salts containing 1, 5, or 8 molecules of water. On examining the present samples it will be seen that this salt has been obtained in 3 degrees of hydration containing 9, 6, and 2 molecules of water respectively, the anhydrous salt being obtained on drying at 150° C.

Dr. W. MARSHALL WATTS. Binocular Spectroscope.

The Binocular Spectroscope might otherwise be described as a spectroscopic opera-glass. It consists of a field-glass, or other form of binocular, in front of the object-glasses of which two exactly similar transparent diffraction-gratings are mounted on optically worked plane-glass. As the instrument has neither slit nor collimator it is applicable, in the first instance, only to luminous objects of definite form, such as vacuum tubes. For ordinary observations of flame-spectra, or spark-spectra, a metal, or ebonite plate, with a slit, in front of the Bunsen or spark is employed. The use of both eyes in spectroscopy constitutes a new departure. The whole spectrum is seen at once, the bright lines stand out in apparent relief, and observations can be made with greater comfort and success, especially with faint spectra.

Sir WILLIAM CROOKES, F.R.S.

1. The Ultra-violet Spectra of the Metals, photographed with a quartz train of five double prisms. The spectrum of pure iron used as a standard.

Aluminium, antimony, arsenic, barium, bismuth, cadmium, caesium, calcium, carbon, cerium, chromium, cobalt, copper, europium, gadolinium, gold, indium, iron, iridium, lithium, lead, magnesium, manganese, mercury, molybdenum, nickel, nitrogen, osmium, palladium, platinum, potassium, praseodymium, radium, rhodium, rubidium, ruthenium, scandium, samarium, silicon, silver, strontium, tantalum, thallium, thorium, tin, titanium, tungsten, uranium, vanadium, ytterbium, yttrium, zinc.

Meteorites.—"Thunda," "See Lasgen," "Narraburra," "Canyon Diablo," "Boogaldi."

Ferro-alloys.—Fe 82.3, Va 13.4, Al 3.2, Si 1.1. Fe 86.6, Va 13.4. Fe 70.9, Va 29.1. Fe 10, Va 90. Fe, Ti. Fe 61.12, Wo 30.5, Cr 8.32. Fe 92.7, Mn 7.3. Fe, Mn. Fe, Si. Fe 25, Si 75.

Steel.—Chrome steel, Cr 3.5 per cent. Nickel steel,

Ni 3.06 per cent. Nickel-chrome steel, Ni 4.08, Cr 1.7 per cent. Tungsten steel, W 3 per cent.

2. Fifty Stereoscopic Photographs, taken by Sir W. Crookes on the occasion of the visit of the British Association to South Africa in the autumn of 1905.

Mr. G. F. HERBERT SMITH. A Refractometer for Liquids.

By means of this compact and portable form of refractometer the refractive indices of liquid and semi-liquid substances may be easily and quickly determined in sodium light to the fourth place of decimals. The attached thermometer gives the temperature at which the readings are taken, and the simple form of water-jacket permits of observations being made at temperatures differing from that of the surrounding air. The range and the degree of accuracy may be varied to suit the particular work for which the instrument is required. The principle of the optical arrangements is identical with that employed in the exhibitor's refractometer for crystals and faceted gemstones. The instrument has been constructed by Mr. J. H. Steward.

Prof. W. F. BARRETT, F.R.S. Entoptiscope, for the Self-examination of Obscurities and Defects within the Eye.

The instrument enables anyone to observe, delineate, and measure an obscurity however minute within the path of the rays in the eyeball, and affords an admirable method for the study of pupillometry of ocular parallax, and of entoptic phenomena generally.

Dr. G. T. MOODY. Specimens illustrating the indifference of Oxygen towards Iron in presence of water, and the effect of the admission of Carbonic Acid.

1. Specimen of soft Swedish iron which has been in contact with air and water both completely freed from carbonic acid for five weeks. During this period approximately 56 litres of air passed over the iron, exposing the metal to a volume of oxygen exceeding thirty times the amount required to completely convert it into ferric oxide.

2. Specimen of the same iron which had remained perfectly bright after exposure for three weeks to water and 32 litres of air, freed from carbonic acid. At the end of the period named, air cleaned by its passage through a tower packed with moist pumice-stone, but containing its normal amount of carbonic acid, was admitted. After seventy-two hours, during which time approximately 16 litres of air passed through, and when considerable rusting had occurred, the tube was sealed.

Prof. WYNDHAM DUNSTAN, F.R.S.

1. New or Rare Minerals from Ceylon.

Many of these minerals have been collected during the progress of the Mineral Survey now proceeding in Ceylon in connection with the Imperial Institute. Others have been found in river gravels sent for examination to the Imperial Institute. These minerals illustrate the wide distribution of thorium in Ceylon.

(1) *Gickelilite*; (2) *Picroilmenite*.—Magnesium iron titanates. These minerals have been investigated at the Imperial Institute and described by Messrs. T. Crook and B. M. Jones in a paper recently contributed to the Mineralogical Society.

(3) *Pleonaste (Ceylonite)*.—A variety of spinel. Iron magnesium aluminates.

(4) *Zirkelite*.—Iron and calcium titanate and zirconate with thorium or uranium dioxides. Some specimens contain as much as 20 per cent of thorium.

(5) *Tscheffkinitite*.—Silicates and titanates of cerium and the allied metals. It contains about 5 per cent of thorium.

(6) *Æschynite*.—Principally niobates and titanates of cerium and the allied metals containing about 5 per cent of thorium.

(7) *Thorianite*.—Principally oxides of thorium and uranium. It contains, as a rule, about 79 per cent of thorium (see *Proc. Roy. Soc.*, 1905).

(8) *Thorianite from Galle*.—This differs from the thorianite previously examined in containing more uranium dioxide, which has replaced some of the thorium. It is

therefore intermediate in composition between thorianite and uraninite. A paper dealing with the composition of this mineral has been recently communicated to the Royal Society by Prof. Dunstan and Mr. B. M. Jones.

(9) *Uraninite*.—Principally oxides of uranium containing also oxides of thorium and other metals. This specimen contains 9 per cent of thorium.

(10) *Thorite*.—Chiefly thorium silicate, containing 70 per cent of thorium.

(11) *Monazite*.—Phosphates of cerium and the allied metals. It contains about 10 per cent of thorium, and is thus richer in thorium than the monazite usually found in Brazil and North Carolina.

(12) *Allanite*.—Silicates of aluminium, iron, calcium, cerium, and the allied metals. It contains 1.5 per cent of thorium.

(13) *Fergusonite*.—Principally yttrium niobate, containing 2 per cent of thorium.

(14) *Sand from Niriella*.—Containing ilmenite, garnet, zircon, rutile, monazite, cassiterite, thorianite, and gold.

2. Minerals from Canada.

(15) *Cobalt, Nickel, and Silver Ore*.—Discovered recently at Haileybury, 227 miles north of Toronto. The minerals present are smaltite, CoAs_2 ; chloanthite, NiAs_2 ; niccolite, NiAs ; cobaltite, CoAsS ; dyscrasite, Ag_3Sb ; erythrine, $\text{Co}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$; annebergite, $\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$; heterogenite, $\text{CoO} \cdot 2\text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$; arsenolite, As_4O_6 ; and native silver.

Dr. P. E. SHAW. An Electrical Measuring Machine.

End standards of length have hitherto been gauged by measuring machines of the Whitworth type. They act by mechanical touch. The chief objections to them are:—1. Since mechanical touch is insensitive, it is impossible to work accurately with definite point contacts, but plane measuring ends are used. These planes are defective as to planeness and as to parallelism with one another. 2. Again, since mechanical touch is insensitive, comparatively large strains are produced in the micrometer screws and nuts at each measurement. 3. No means are provided by which the experimenter can adjust or calibrate the machine as he should do when it arrives from the maker and periodically afterwards. In the electric machine it is claimed that each of the above objections is avoided for:—1. Electric touch provides great sensitiveness, and point-to-point contact is possible. 2. No false assumptions are made as to perfection of the plane faces. 3. Strain in the machine is negligible. 4. Each part of the machine can be adjusted. The errors in gauges are measured by this machine. In some cases they are considerable.

Prof. SILVANUS P. THOMPSON, F.R.S., exhibited and described the Electric Production of Nitrates from the Atmosphere.

Various processes have been devised for the synthesis of the nitrogen and oxygen of the atmosphere by means of electric discharges. These all start from the original observations of Cavendish in the years 1781 and 1786. Recently there have been established commercial processes for the electric production of cyanamide by the process of Dr. Frank, and of calcium nitrate by the process of Birkeland and Eyde. The latter has been at work for over a year at Notodden, in Norway. The special feature is the furnace in which the synthesis is effected, the electric discharges being produced by alternating currents at about 3000 volts between copper electrodes placed between the poles of a large electromagnet. There results a roaring disc of flames about 6 feet in diameter, through which air is gently flown. The nitrous vapours with which the air is thus charged are passed through absorbing towers, where they are absorbed in water and in quicklime, the whole of the products being converted into calcic nitrate which is concentrated. The product is used for agriculture (being equal in value to Chili saltpetre) and in the dye-stuff industry. The power is furnished by waterfalls. One kilowatt may be taken as able to produce 500 kilogrms. of nitrate, at least, per annum.

CORRESPONDENCE

THE TEMPERATURE OF SOLUTIONS HEATED BY OPEN STEAM.

To the Editor of the Chemical News.

SIR,—Might I point out in reply to Mr. Frank Spence (CHEM. NEWS, xciii., 68) that in the *Reports of the British Association*, 1869 and 1870, in which Mr. Peter Spence's experiments are described and to which my reference applies, no theoretical explanation of the phenomenon in question is given. That this was subsequently published in the *Brit. Mer. Gazette* in 1878 was not known to me, but in any case that journal can hardly be considered a suitable medium for the publication of scientific information.

I did not state that the first person to theoretically explain the matter was Dr. Claassen. What I said was that Dr. Claassen's paper contained the only other reference thereto which I had seen.

Since my paper was published I have seen a number of other references to the subject which it may be of sufficient interest to quote. These are:—"Watts' Dict. of Chem.," 1881, vol. viii., Pt. II., Third Suppl., p. 947; "On Steam and Brines," J. Y. Buchanan, F.R.S., *Trans. Roy. Soc. Edinb.*, 1898-9, xxxix, iii., p. 529; "Physical Chemistry," James Walker, 1901, p. 84. In the above volume of "Watts' Dictionary" it is stated that "the heating of saline solutions to their boiling-points by the action of aqueous vapour at 100° was noticed more than fifty years ago by Faraday and by Gay-Lussac" (*Ann. Chim. Phys.*, 1822).

Mr. Peter Spence deserves all credit for his independent discovery, and it is surprising that so striking and interesting a phenomenon is so little known amongst chemists generally.—I am, &c.,

THOS. STEEL.

Sydney, New South Wales.
April 2nd, 1906.

NOTICES OF BOOKS.

Practical Electrochemistry. By BERTRAM BLOUNT, F.I.C., Assoc.Inst.C.E. Second Edition. London: Archibald Constable and Co., Ltd. New York: The Macmillan Company. 1906.

THE second edition of this work has been entirely brought up to date and enlarged to a considerable extent, the descriptions of many new processes and of modifications of old methods having been added. For instance, we may mention the new section on the electro-metallurgical production and treatment of iron and steel, in which region during the last five years the earlier experimental difficulties have been overcome, so that the industry bids fair to become one of great importance. Thus the book now gives a thoroughly complete and systematic survey, from the most modern point of view, of the principles and practice of all the most important electrochemical processes employed industrially, and, as in the former edition, the practical aspect of the advantages to be gained by the use of electrochemical methods is emphasised.

Physical Chemistry for Electrical Engineers. By J. LIVINGSTON R. MORGAN, Ph.D. First Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1906.

THIS book is intended especially for those who wish to acquire a slight knowledge of physical chemistry in as short a time as possible, and as far as it goes it appears to fulfil its purpose. The difficulty of writing such a

sketch of a wide subject has been surmounted on the whole successfully by the author, whose work shows plain traces of his indebtedness for many of his ideas and explanations to Prof. Ostwald's "Vorlesungen über Naturphilosophie." The book will perhaps serve as an introduction to the study of larger and more complete works on the same subject, although it is hardly interesting enough to awake much enthusiasm in a beginner. Certain important branches, e.g. solutions, are treated comparatively fully, and the collection of problems will be found useful in consolidating the student's knowledge of the general principles of physical chemistry. The addition of an index would add to the value of the book.

The Origin of Life. By JOHN BUTLER BURKE. London: Chapman and Hall, Ltd. 1906.

GREAT interest was aroused, especially among the general public, when the results of Mr. J. B. Burke's experiments were first announced some months ago, and it seems likely that this book which he has just published, giving further information on the same subject, will be purchased and read by a wider and less highly trained circle of readers than that which generally concerns itself with scientific works. It is to be feared that the uninitiated reader will close the book without having acquired a very high opinion of it as a contribution to our knowledge of the physical basis of life. He will have read a large amount of theoretical discussion, especially in regions in which speculation is safe and contradiction impossible, but he will have learned very little more precise information about those mysterious radiobes than was to be gathered from the first articles in which they were described. The test of the vitality of the radiobe is, in the author's opinion, the stoppage of growth and the beginning of the disintegration process; and since special emphasis is laid upon this latter phenomenon, we might expect to find details and definite measurements, which, however, we look for in vain. While the author displays a powerful imagination, without which the scientific investigator cannot hope to proceed very far, he appears to be unable to present theory and fact to his readers so that a sense of the true proportion between them is maintained, and when he elaborates his theory, claiming that some of the processes of nature have been imitated by the artificial production of cells, and that he has found the bridge between the organic and inorganic worlds, we feel that he is basing an unwieldy and top-heavy structure upon a shallow and inadequate foundation.

Petrogenesis ("Petrogenesis"). By Dr. C. DOELTER. Braunschweig: Friedrich Vieweg und Sohn. 1906.

THIS book is the thirteenth of the series of monographs on scientific and mathematical subjects, "Die Wissenschaft." The author has a very wide knowledge of petrography and mineralogy, and has prepared an exhaustive treatise on the origin of rocks, dealing first and most fully with eruptive formations, and then passing to crystalline schists and sedimentary deposits. The great advances which have recently been made in our knowledge of the origin of rocks are to be ascribed to the spread of the use of the methods of physical chemistry, and these are treated at length, the experimental parts of the subject being made especially prominent. The question of the nature of rocks can be satisfactorily explained only when the mineral constituents and the chemical composition have been thoroughly investigated in conjunction with the geological occurrence, and these subjects the author is thoroughly competent to deal with in the most enlightened spirit. A pleasing feature of the book is the full recognition of the work of the geologists and chemists of all nations, periodical literature in many languages having been carefully studied and abstracted, so that a most comprehensive survey of the whole subject is given.

Microscopes and Microscopical Accessories. Jena: Carl Zeiss. 1906.

THE thirty-third catalogue issued by the firm of Carl Zeiss contains details of the objectives and oculars, stands, and accessory apparatus, manufactured by this famous firm. Many new forms of stands are advertised, among them a simpler kind for laboratory use, to which we may call special attention, and large reductions are notified in the prices of achromatic objectives, Huygenian oculars, &c., while in the case of ruled gratings and heating chambers, slight advances have been made in the prices. Magnifiers and dissecting stands are not included in this list, a special catalogue of them having been issued. All those who are contemplating buying a microscope or accessories should make a point of consulting this list, which is fully illustrated, and contains specifications of complete outfits as well as information relating to all kinds of separate pieces of microscopical apparatus. We understand that Messrs. Zeiss will forward a Catalogue to any of our readers who apply for the same.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 16, April 17, 1906.

Pure Ferro-molybdenums.—Em. Vigouroux.—In a recent paper the author describes two general methods of preparing pure ferro-molybdenums. He now investigates their composition and properties. The residue, Fe_3Mo_2 , which remains when two of the alloys are exhausted in the cold, either by hydrochloric acid or copper chloride in hydrochloric solution, has a density of 9.16, and is non-magnetic. The body FeMo , which can be separated from alloys containing between 54 and 63 per cent of Mo, has a density 9.01, and is also non-magnetic. It becomes incandescent in chlorine at 285° , and in oxygen at a red heat. FeMo_2 can be isolated from alloys containing between 64 and 67 per cent Mo, and has density 9.41.

Characteristic Reaction of Ethyl Glyoxylate. Action of Ammonia on this Ether and its Derivatives. —L. J. Simon and G. Chavanne.—Ethyl glyoxylate, under the action of pure aqueous ammonia, gives a precipitate which is white at first, and, after passing through various tints, finally becomes bluish black. At the same time the ammoniacal liquor becomes dark red. This succession of colorations takes place rapidly when the liquid is hot and slowly when cold. When the ethyl glyoxylate is present in very small quantity the liquid remains limpid, but even traces of ether bring out the colour. Ammonia can be replaced by its carbonate, CO_2 being evolved during the reaction. The coloration is due to a black substance which the authors isolate and analyse: $2\text{COH} \cdot \text{CO}_2\text{C}_2\text{H}_5 + 3\text{NH}_3 = 2\text{C}_2\text{H}_5\text{OH} + \text{C}_4\text{H}_9\text{N}_3\text{O}_4$. It is found to be a true ammoniacal salt.

Acid Properties of Amidon.—E. Demoussy.—The author's experiments show amidon to have all the characteristics of a weak acid. It may be compared with carbonic acid, in that it resembles the other hydrates of carbon. Similarly, it contracts with the metallic hydrates of compounds dissociable with water, and will absorb small quantities of neutral salts. These properties probably assist in the absorption of mineral matters by plants, and particularly contribute to the mineralisation of organisms containing amyl reserves.

No. 17, April 23, 1906.

The Diffusion of Solutions and their Molecular Weights.—Michel Yégonow.—In order to determine the velocity of movement of oxygen and hydrogen sulphide in nutritive media, and also in water for micro-biological researches, and finding no direct method, the author was obliged to attack the problem indirectly. He first supposed that definite relations can exist between the coefficient of diffusion (K) and the velocity of movement (v) in a given section for solutions having the same osmotic pressure; that is to say, equimolecular solutions. He makes experiments on pure absolutely transparent 10 per cent gelatin solution, and finds (1) that the proportion between the coefficient of diffusion (K) and the velocity of motion (v) is a constant for equimolecular solutions of all substances; (2) that when the concentration (x) varies in geometric progression the velocity v varies in arithmetic progression.

Atomic Weight and Spark Spectrum of Terbium.—G. Urbain.—The author has previously explained his method of isolating terbium in a state of purity, and has also shown that he was unable to assign a characteristic spectrum to this body. In order to determine the atomic weight of terbium he estimates the water in the octohydrated sulphate $(\text{SO}_4)_3\text{Tb}_3 \cdot 8\text{H}_2\text{O}$. His numbers are very concordant, and the mean of five experiments is 159.22 if O = 16. A further examination of the spark spectrum shows it to be very rich in lines. The most characteristic are given in a table.

Estimation of Cadmium in Volatile or Organic Salts.—H. Baubigny.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Reviving Faded Ink.—I should be greatly obliged for particulars of any chemical which will revive (if only temporarily) red and black ink. I have a very old document (parchment), and the writing, which is in both red and black ink, has in many places quite faded away.—S. G. W. MANN.

MEETINGS FOR THE WEEK.

MONDAY, 21st.—Society of Arts, 8. (Cantor Lectures). "Heraldry in relation to the Applied Arts," by George W. Eve.

— Society of Chemical Industry, 8. "The Problem of the Electro-chemical Fixation of Nitrogen," by P. A. Guye.

TUESDAY, 22nd.—Royal Institution, 5. "Glands and their Products," by Prof. William Stirling, M.D., &c.

WEDNESDAY, 23rd.—Society of Arts, 8. "The General Supply of Electricity for Power and other Purposes," by James N. Shoolbred, B.A.

THURSDAY, 24th.—Royal Institution, 5. "Man and the Glacial Period," by Prof. W. J. Sollas, F.R.S.
— Society of Arts, 4.30. "The Persis of Persia," by Major Percy Molesworth Sykes.

FRIDAY, 25th.—Royal Institution, 9. "Compressed Air and its Physiological Effects," by Leonard Hill, M.B., F.R.S.

— Physical, 5. "Colour Phenomena in Photometry," by J. S. Dow. Exhibition of an Automatic Arc Lamp, by H. Tomlinson and Rev. G. T. Johnston. "Theory of Moving-coil and other kinds of Ballistic Galvanometers," by H. A. Wilson. Exhibition of Bifilar Galvanometer free from Zero Creep, by A. Campbell.

SATURDAY, 26th.—Royal Institution, 3. "The Old and the New Chemistry," by Prof. Sir James Dewar, D.Sc., F.R.S., &c.

THE CHEMICAL NEWS.

VOL. XCIII., No. 2426.

ON THE DISTRIBUTION OF RADIUM IN THE EARTH'S CRUST, AND ON THE EARTH'S INTERNAL HEAT.*

By the Hon. R. J. STRUTT, F.R.S., Fellow of Trinity College, Cambridge.

1. Introduction.

PROFESSOR RUTHERFORD has given a calculation which suggests that there may be enough radium in the earth to account for the temperature gradient observed near the surface ("Radio-activity," p. 494, 2nd Edition).

The question is of great interest from a cosmical point of view. For if we find that the earth's internal heat is due to radio-activity, and if we assume, as has been usual, that this heat is due to some vestiges of the cause operative in the sun and stars, it would follow that these latter are heated by radio-active changes also.

Prof. Rutherford's calculation was based on some data given by Elster and Geitel on the amount of radium emanation which diffused out from a sample of clay. These data were obtained at a time when the quantitative determination of minute amounts of radium was not well understood, and are, moreover, inadequate to give any general idea of the average amount of radium in the earth's crust. I have therefore made an extensive investigation of the amount of radium in various representative rocks. This forms the subject of the present paper. The results are very surprising. Considerable detail will therefore be given in order to enable readers to judge whether there is any probability of these results being substantially incorrect.

2. Choice of Material.

The earth's crust, which is alone accessible to us, consists of igneous rocks, and of sedimentary material which results from the action of geological changes upon these rocks. No doubt the average radium content of the original igneous rocks might be inferred fairly well from the examination of a large number of sedimentary ones. It is, however, much more satisfactory to examine the igneous materials directly, for then they can be classed among themselves as to their radium content.

I have examined a few sedimentary rocks, but do not attach much importance to them, and rely chiefly on results obtained with original igneous material for determining the average radium content of the earth's crust. The results with regard to sedimentary rocks will be given in a future paper. I hope also to determine which of the numerous minerals contained in igneous rocks carry the radium, a subject not touched in the present communication.

Meteorites have a special interest of their own. A few determinations have been made on them, and are incidentally included in this paper.

3. Method of Determining Radium Content.

Radium in the rocks was quantitatively determined by means of its emanation. A solution of the rock was stored till the emanation had accumulated. This latter was then extracted by boiling, and introduced into an electroscope. The increased rate of leak produced was a measure of the amount of radium present. This measure was made absolute by going through the same process with a uranium mineral of known radium content.

In order to make certain of extracting the emanation quantitatively, it is essential to decompose the rock completely by chemical agency. In the case of limestones and

metallic meteorites, this can be effected by solution in hydrochloric acid, but in the case of siliceous materials, fusion with alkaline carbonate is necessary.

The standard procedure was as follows:—Fifty grms. of the rock was broken up in an iron mortar, and then finely ground in an agate one, until it would pass through a sieve of 90 threads to the inch. This process could be carried out by an unskilled assistant in less than an hour, and ensure easy decomposition of the rock.

Two hundred and fifty grms. of a mixture of anhydrous sodium and potassium carbonates was melted in a large platinum basin. For this purpose the basin was surrounded with an extemporised furnace casting of asbestos millboard, and heated from below by means of a gas blowpipe. The blowpipe was supplied with air from an automatic blowing apparatus worked by water pressure. As soon as the carbonate was melted, the rock powder was thrown on to its surface in small portions at a time until it had all been added. The fusion was usually continued for about an hour after all effervescence was over.

The residue was then digested with hot water to dissolve out the alkaline silicates and carbonates. The portion insoluble in water was dissolved in hydrochloric acid. Some silica always separated from the acid solution, and was allowed to remain floating in it.

The two solutions, aqueous and acid, were set aside in separate flasks closed with indiarubber stoppers. Mixing them was avoided, because of the bulky and unmanageable precipitate of silica which would have been thrown down.

Decomposition with hydrofluoric acid has some advantages over the use of sodium carbonate. It requires, however, more minute pulverisation of the material, and is more costly in practice owing to difficulties of carriage and storage. After one or two trials its use was abandoned.

The two flasks containing the respective solutions were allowed to stand for some determinate number of days. A week was the minimum. More commonly a fortnight or three weeks was allowed. During this time, any radium contained in the rock was generating emanation. After three weeks the quantity has practically reached a maximum. The fraction of this maximum generated in any lesser period could be calculated from the equation for the rise of activity, originally given by Rutherford and Soddy.

I described a method for quantitatively extracting the emanation in *Proc. Roy. Soc.*, 1905, A, vol. lxxvi., p. 89. An improved modification of that method has been employed in the present investigation. The flask A (see figure) contains the solution. The accumulated emanation is at first partly dissolved, partly contained in the air which occupies the upper part of the flask. The flask is uncorked and attached to the lower end of the condenser B as rapidly as possible, so as to avoid loss of emanation. A is then boiled to expel radium emanation. The steam which issues is condensed in B, and drops back. The air charged with emanation passes out into the gas-holder C, displacing the water which previously filled it. This boiling is continued for one hour. At the end of that time, the cooling water is run off from the jacket of B. Steam is allowed to pass so as to wash out all air and emanation from A, and from the connecting tubes into C. The indiarubber connection at D is then nipped,* and the burner under the flask immediately withdrawn.

In this way the emanation is collected in the gas-holder C. It merely remains to transfer it to the electroscope when cold. The latter is exhausted, and the emanation allowed to pass into it through the stopcock E and a drying tube. Air is then admitted to the electroscope up to atmospheric pressure. After an interval of three hours, to allow the active deposit to form, the rate of leak is read.

The normal leak of the electroscope was repeatedly determined in the course of the investigation.

The following are the values in scale-divisions per hour:—24, 25·3, 24·1, 24, 23, 20·6, 21·7, 22·3, 22·5, 22·1;

* A Paper read before the Royal Society, April 5, 1906.

* To do this conveniently, it is very desirable to have the pinchcock attached to a firm support, so that it can be screwed up with one hand.

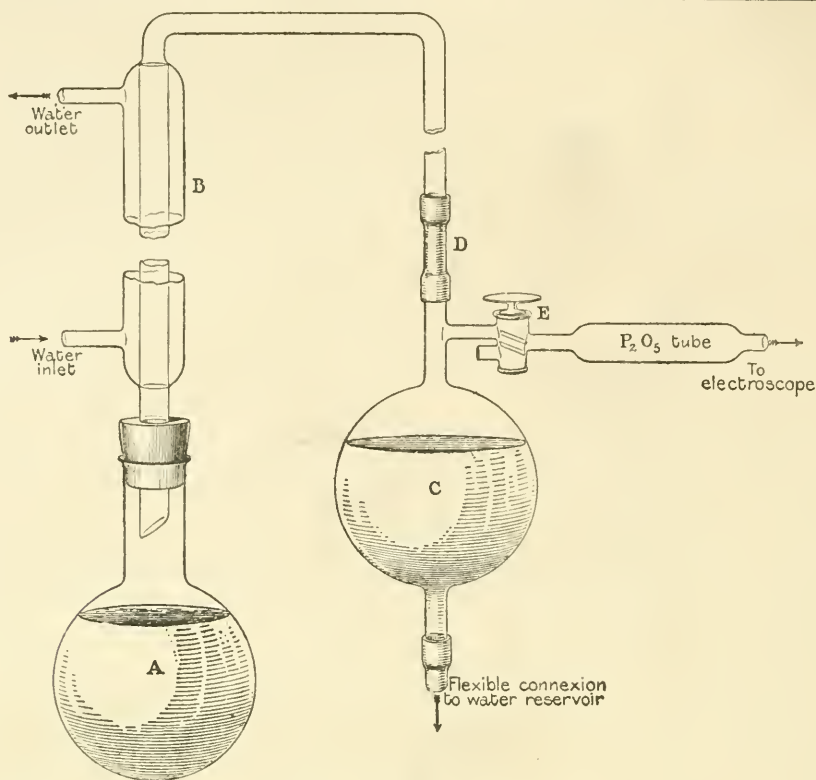


FIG. 1.

TABLE I.—Standardisation Experiments.

Mineral.	Percentage of uranium (metal).	Quantity (gram.).	Rate of leak* due to emanation accumulated in one day.	Constant deducted.
Torbernite	51.0	0.0076	214.0	2.3 × 10 ⁻¹²
Torbernite, same sample	51.0	0.0076	209.0	2.36 × "
Torbernite	51.0	0.0046	116.5	2.56 × "
Torbernite, same sample	51.0	0.0046	113.0	2.64 × "
Pitchblende	62.4	0.0063	207.0	2.41 × "
Pitchblende, same sample	62.4	0.0063	202.0	2.45 × "

* Corrected for normal leak of the electroscope.

mean, 23 nearly. These values were taken soon after exhaustion of the electroscope and admission of air.

If the instrument was left closed, the leak was found to have risen appreciably after the lapse of a day. A similar effect has been noticed at the Cavendish Laboratory, and is, I believe, under investigation there. It does not come into question here, since time was never allowed for it to enter.

In work of this kind, when the effect to be looked for is small, it is most necessary to make certain that the emanation really comes from the material under investigation, and not from any extraneous source. I was deceived in this way in concluding that mercury gave off an emanation. In the present case every precaution was taken.

The laboratory had never had radio-active materials introduced into it. Solutions of the reagents employed were separately tested for emanation, after they had stood closed for a fortnight, with the following results:—

	Rate of leak.
Sodium carbonate, 250 grms.	23.9
Potassium carbonate, 250 grms. . . .	24.2
Hydrochloric acid, 500 c.c.	24.0
Water (Cambridge supply), 2000 c.c. .	24.0

In none of these cases does the leak measurably exceed that normal to the electroscope. It may therefore be concluded that the reagents used to decompose the rocks are not responsible for the emanation obtained.

Cambridge tap-water was used to make the solutions and to fill the gas-holder c (figure). This water originally contains dissolved emanation, as Professor J. J. Thomson has shown. It was therefore carefully boiled to expel this before use. The test given above was made on water which had already been boiled before setting it aside, and shows that no measurable quantity of emanation is generated by dissolved material when the original supply has been expelled. The (boiled) water in the gas-holder was changed after each experiment.

Rutherford and Boltwood have determined the radium content of uranium minerals in absolute measure (*Am. Journ. Sci.*, 1905, p. 55). They find that the radium associated with 1 gm. of uranium is 7.4×10^{-7} gm. I use this value rather than my own, because they tested the heat production of their standard radium, while I had no test for the purity of mine (*Proc. Roy. Soc.*, 1905, A, lxxvi., p. 88).

The uranium minerals used for standardisation were

torbernite (copper-uranium phosphate), containing 60 per cent U_3O_8 (= 51 per cent uranium), and pitchblende, containing 73.5 per cent U_3O_8 (= 62.4 per cent uranium).

The rate of leak due to the emanation produced by a few m.grms. of each of these in *one day* was determined. From this the quantity of radium was deduced, which would in an *indefinite time* produce enough emanation to give a leak of one division per hour. This is the constant given in the last column of Table I.

The mean value for the constant is 2.45×10^{-12} ; or, in other words, a leak equal to one scale-division per hour represents 2.45×10^{-12} grm. of radium in the sample examined, if the latter has had time to produce its maximum amount of emanation.

Two specimen determinations will now be given in detail, the first of granite from the Cape of Good Hope, the second of olivine rock from the Isle of Rum. These are respectively representative of high and low radium content.

Cape Granite (50 grms.).—Solutions stood from March 21 to March 26, giving 60 per cent of the maximum amount of emanation.

	Scale-div. per hour.	Corrected.
Emanation from acid solution ..	103	80.0
Emanation from alkaline solution .	31	8.0
Total	88.0 scale-divisions per hour.	

Thus the equilibrium amount of emanation would give 146 scale-divisions per hour, or per grm. of rock $\frac{146}{50} = 2.92$ scale divisions per hour. Thus 1 grm. of rock contains $2.92 \times 2.45 \times 10^{-12}$ grm., or 7.15×10^{-12} grm. radium.

Olivine Rock, Isle of Rum (50 grms.).—Solutions stood from January 31 to February 19, giving practically the equilibrium amount of emanation.

	Scale-div. per hour.	Corrected.
Emanation from acid solution ..	34.0	11.0
Emanation from alkaline solution .	25.8	2.8
Total	13.8 scale-divisions per hour.	

One grm. of rock would give 0.276 scale-divisions per hour, and contains $2.45 \times 0.276 \times 10^{-12} = 0.676 \times 10^{-12}$ grm. radium.

This last example represents, as mentioned above, nearly the lowest radium content encountered among igneous rocks. It will be noticed that the leak produced by the emanation is, even in this unfavourable case, about half that normal to the electroscope, and is, therefore, quite well marked. It will be noticed also that the alkaline solution contains only a small proportion of the total radium present in the original rock.

(To be continued).

A REVISION OF THE ATOMIC WEIGHTS OF SODIUM AND CHLORINE.*

By THEODORE WILLIAM RICHARDS
and
ROGER CLARK WELLS.

(Continued from p. 230).

THE RATIO OF SODIC TO ARGENTIC CHLORIDE (*continued*).

In most experiments the residue of asbestos shreds was found, after ignition, to contain a trace of silver. This was undoubtedly produced from the decomposition of silver chloride during ignition, the latter salt having passed through the Gooch as exceedingly fine particles or having precipitated, in time, upon the asbestos shreds. The amount of this silver, as well as the amount of asbestos shreds, varied according to the efficiency of the Gooch mat and the fineness of the holes of the Gooch filter—the smaller those holes the better. The loss of chlorine upon ignition was determined in sixteen experiments, chiefly in those upon the

synthesis of silver chloride. This was done by determining the trace of reduced silver by Volhard's process, using 1/100 normal solutions. The average of determinations, which varied from 0.00 to 0.07 m.grm., amounted to only 0.02 m.grm.; this correction was applied. Although negligible, its magnitude had to be determined in order that one might be assured of safety in neglecting it.

With the asbestos at our disposal, the prepared Gooch crucible was not at all hygroscopic. An hour's standing in the balance case had no effect upon its weight. Even upon ignition, the mat, weighing less than 0.03 grm., lost only a negligible amount—and it was never heated above 150° in the actual analyses.

As has already been said, no chloride could be found by the nephelometer in any of the wash waters containing any considerable amount of argentic nitrate. Hence, after filtration through the small filters, these were cast aside and the small solubility correction of 0.03 m.grm. per litre applied to them.

The next two or three wash waters, containing only small amounts of nitrate, were collected separately, because they contained traces of chloride also. The subsequent wash waters—free from nitrate, but containing much chloride—were all united. The chloride in both separate portions was carefully determined by means of the nephelometer—that is, by comparison of opalescence. The two portions, one containing traces of argentic nitrate and one free from salt, must be estimated separately, because if all the wash waters are mixed together the opalescence usually occurs prematurely—a circumstance which interferes with the accuracy of the nephelometric comparison.

The amount of silver chloride thus found in the wash waters was added to the weight of that collected on the Gooch crucible.

Any accidentally included foreign substance—for example, silica from the glass-stoppered flasks, dust from the air, or occluded sodic nitrate—which would make the obtained weight of silver chloride too great, would make the computed atomic weight of sodium too low. Since our results were lower than Stas's, particular attention was paid to these and similar possibilities. One question especially seemed to demand an answer, namely, that concerning the possibility of the abrasion of powdered glass from the ground-glass stopper of the precipitation flask.

A newly-ground stopper sheds glass noticeably. It must always be polished and rubbed a long time until the loose particles are thoroughly dislodged. A flask of soft glass never ceases to grind away slightly every time the stopper is inserted. The large 2-litre Erlenmeyer flasks used in the final experiments were of very hard insoluble glass, with rather wide necks, very suitable for precipitation and for washing. In order to test the extent of their abrasion, one of the stoppers was removed and replaced a hundred times. The resulting powdered glass was collected on a small fine filter and found to weigh 0.2 m.grm. Since, during a single determination, the stopper was not replaced over a dozen times, it is safe to infer that the error from this cause could not have exceeded 0.02 m.grm.—a negligible quantity.

Other sources of contamination were so carefully guarded against that they can hardly have been present.

The foregoing general description may be profitably illustrated by recounting the details of a single experiment before the results of all the experiments are given.

Experiment 63 (April 5, 1904; Salt J).

	Grms.
Corrected excess weight of crucible over counterpoise	0.19994
Corrected excess crucible plus fused salt over counterpoise	5.76754
Weight salt in air ($24^\circ 764$ m.m.)	5.56760
Vacuum correction	+0.00231

Weight of sodic chloride in vacuum .. 5.56991

* Published by the Carnegie Institution of Washington, April, 1905.

As a suitable excess of silver nitrate, 16.40 grms. were taken for precipitation. The concentration of the silver salt being about fifth normal and that of the sodic salt not much greater, the total mother-liquor was 1.4 litres. Five washings of the precipitate were made after it had stood over night, with 0.2-litre portions of water containing about 0.05 gm. of silver nitrate per litre. Washings Nos. 6 and 7 were made with pure water and collected separately. Washings 8 to 12 were made with slightly acidified water and collected separately. The whole precipitate was finally washed upon the Gooch crucible. After drying it appeared perfectly white.

	Grms.
Corrected excess weight Gooch crucible (dried at 150°) over counterpoise	0.21709
Corrected excess weight crucible and AgCl (dried at 150°) over counterpoise	13.87382
Weight of silver chloride in air	13.65673
Vacuum correction	+0.00100
Weight of unfused AgCl in vacuum	13.65773

The mother-liquors and wash water were passed through a small filter, which was ignited in a small porcelain crucible.

	Grms.
Corrected excess porcelain crucible over counterpoise	0.42525
Corrected excess, plus residue and ash	0.42535
Residue and ash	0.00010
Ash	0.00001
Residue, asbestos shreds	0.00009
Loss of chlorine during ignition (see p. 230)	+0.00001

Total residue 0.00010

A large portion of the silver chloride, 10.50 grms., was fused in a small approximately counterpoised crucible weighing about 8 grms.

	Grms.
Corrected excess crucible, plus AgCl, over counterpoise (a)	10.64846
After fusion, corrected excess over counterpoise	10.64769
Loss of 10.50 grms. AgCl on fusion	0.00077

Hence loss of total AgCl = $\frac{13.66}{10.50} \times 0.00077 = 0.00100$.

(a) In this case the counterpoise contained no argentic chloride, but in the most careful experiments the counterpoise contained as much of this salt as the test crucible.

The nephelometer revealed no chloride in the mother-liquor and first five washings; the correction of +0.07 m.grm. was applied for this solubility even in the presence of the excess of silver nitrate.

Washings Nos. 6 and 7, volume 0.220 litre in all, were found to have a trace of chloride, and its amount was estimated by the nephelometer, making comparison with two different standard tubes.

The factor for converting 1 millilitre of standard solution in a nephelometer tube into silver chloride per litre was 0.047. (See Table, next column).

For 220 cubic centimetres the weight of dissolved AgCl is $\frac{220}{1000} \times 0.00028 = 0.00006$ gm.

Similarly for washings Nos. 8 to 12 (0.94 litre) was found on the average 0.00146 gm. of argentic chloride per litre (the individual determination being 1.47, 1.41, 1.54, and 1.44 m.grms.). For 940 cubic centimetres we have $\frac{940}{1000} \times 0.00146 = 0.00137$ gm., and hence the total

Standard tube containing NaCl solution (c.c.).	Time of forming opalescence.	Heights of opalescences appearing equal. Wash Standard. waters.		Ratio of heights.	Soluble silver chloride.
0.02	15 mins.	30	100	0.30	$0.30 \times 0.02 \times 0.047 = 0.00028$ gm. per litre.
0.005	7 mins.	100	80	—	$1.18 \times 0.005 \times 0.047 = 0.00028$ gm. per litre.
	9 hrs.	100	85	1.18	

dissolved silver chloride = $0.00007 + 0.00006 + 0.00137 = 0.00150$.

Altogether we now have for the total weight of argentic chloride:—

	Grms.
Weight of argentic chloride (vacuum) in crucible	13.65773
Asbestos, &c., washed through Gooch crucible	+0.00010
Dissolved	+0.00150
Loss of fusion	-0.00100

Corrected weight of argentic chloride .. 13.65833

Ratio,—

AgCl : NaCl = 13.65833 : 5.56991 = 100.000 : 40.7803.

Molecular weight NaCl (if Ag = 107.93 and Cl =

35.455) = 40.7803×143.385 58.473

Assumed atomic weight Cl 35.455

Hence atomic weight Na 23.018

Most of the following determinations were essentially similar to this, but a few small differences should be noted. In Experiment 27 the eight washings were extended over five days. In Experiment 64, which must be considered as the best single experiment of all, the concentrations were lowered to tenth normal, and twelve washings were made, the first within three hours, the last after a day's lapse. Considerable nitric acid was added to the first seven wash waters. The slightly higher result of this experiment probably indicates diminished occlusion of sodic nitrate.

Three experiments were rejected, two because blackening of the argentic chloride showed that the argentic nitrate in the first wash waters had not been eliminated by the subsequent washing with pure water, and one because of known loss of argentic chloride. These oppositely erring results would have no effect on the final average if they had been included; but in such a table as this it seems advisable to include only results not vitiated by known sources of error. In the following table are given the final data and results of this comparison of argentic and sodic chlorides.

The Ratio of Sodic and Argentic Chlorides. Final Series.

Expt.	Prep.	Weight NaCl (in vacuo). Grms.	Weight AgCl (in vacuo). Grms.	Parts NaCl equal to 100,000 parts AgCl.
13.	K	3.27527	8.03143	40.781
19.	B	5.56875	13.65609	40.779
20.	A	4.18052	10.25176	40.779
22.	C	4.54319	11.14095	40.779
23.	D	1.97447	4.84196	40.778
27.	E	3.97442	9.74547	40.782
61.	H	6.60495	16.41725	40.780
62.	I	2.88692	7.07955	40.778
63.	J	5.56991	13.65833	40.780
64.	J	5.85900	14.36693	40.781
		44.52740	109.18972	Aver. 40.780

If the atomic weight of silver is taken as 107.930, and that of chlorine as 35.455, the atomic weight of sodium, calculated from the above average, will be 23.017—a result 0.14 per cent lower than Stas's.

In spite of every effort to detect some error tending to diminish the atomic weight of sodium, and thus to cast doubt on this low value, and in spite of increasing precautions and increasing skill in the details of the experimentation, the last results are no higher than the very first one. Hence further prosecution of this method seemed to be of no avail. The reason for the difference between this value 23.017 for the atomic weight of sodium and Stas's 23.048 is best discussed after the results of the comparison of sodic chloride with metallic silver have been detailed.

(To be continued).

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

PART II.—ANALYSIS OF THE TUNGSTEN GROUP.

By ARTHUR A. NOYES.

(Continued from p. 227).

Confirmatory Experiments and References.

G. D., § 4.—See C. E., P. 35, N. 4, in regard to the separation of tungsten from titanium by digestion with $(\text{NH}_4)_2\text{S}$, and C. E., P. 38, N. 5, in regard to that by fusion with Na_2CO_3 and S.

For the separation of tungsten and titanium by fusion with KNO_3 and K_2CO_3 , see Defacqz, *Comptes Rendus*, 1896, cxxiii., 823.

A mixture of 10 m.grms. W and 300 m.grms. Ti in HF solution was treated by P. 33, 35, 36, and 38, except that the fusion with Na_2CO_3 and S was replaced by the following process:—The NH_4OH precipitate obtained after the treatment with H_2O_2 , and the evaporation with H_2SO_4 was ignited in a platinum crucible and mixed with eight times its weight of eight parts KNO_3 and two parts K_2CO_3 , the mixture kept at a dull red heat for thirty minutes; the mass was treated with water, the water evaporated off, the residue again treated with water, and the liquid filtered. The residue was dissolved in H_2O_2 and HCl, the solution evaporated with H_2SO_4 , and, after dilution, poured through a Zn column into HgCl_2 solution; no precipitate resulted. The filtrate was strongly acidified with HNO_3 and evaporated to dryness; the mass was treated with water, the solution filtered, and the (white) residue treated with NH_4OH ; only a small portion of it dissolved, but the solution, on acidifying with HNO_3 , gave a small precipitate of H_2WO_4 (1 to 2 m.grms.); the white residue gave no colour when heated with H_2O_2 and HCl.

The experiment was repeated with a mixture of 300 m.grms. W and 300 m.grms. Ti; a large grey precipitate was produced in the HgCl_2 solution after the NH_4OH precipitate had been fused with KNO_3 and K_2CO_3 .

G. D., § 5.—100 m.grms. Ti in one experiment, 5 m.grms. Nb in a second, and a mixture of 100 m.grms. Ti and 5 m.grms. Nb in a third, as oxides, were dissolved in HF, the solution evaporated three times with HNO_3 , the residue heated thirty minutes at 120° , and then warmed with 10 c.c. 3 per cent H_2O_2 and 1 c.c. HNO_3 (1:20); the TiO_2 and also the mixture of TiO_2 and Nb_2O_5 dissolved completely, but the pure Nb_2O_5 did not seem to dissolve at all.

500 m.grms. Ti (as H_2TiO_3) were dissolved in HF, the solution evaporated just to dryness with HNO_3 , the residue moistened with HNO_3 , and the latter evaporated off; 10 c.c. 3 per cent H_2O_2 and 2 c.c. HCl (1:12) were added, and the mixture heated to the decomposition-

temperature of the H_2O_2 ; in three minutes everything had dissolved. The same experiment was repeated with 2 m.grms. Nb as Nb_2O_5 , and in a separate experiment with 2 m.grms. Ta as Ta_2O_5 ; most, if not all, of the substance remained undissolved in each case, even on five to ten minutes' heating. The experiment was again repeated with a mixture of 12 m.grms. Nb and 100 m.grms. Ti; everything dissolved on three minutes' heating except a few hard flakes, and these went into solution on heating for five minutes longer. It was also repeated with a mixture of 5 m.grms. Ta and 100 m.grms. Ti; the whole residue went into solution in five minutes. It was repeated with 500 m.grms. Ti, except that no HCl was at first added with the H_2O_2 ; the residue dissolved much more slowly, and some still remained after ten minutes, but this dissolved at once on adding 2 c.c. HCl (1:12).

For the separation of titanium and uranium from iron by alkaline H_2O_2 , see P. H. Walker (*Journ. Am. Chem. Soc.*, 1898, xx., p. 515).

To a solution in 5 c.c. H_2SO_4 (1:20) of 100 m.grms. Ti in one experiment, and of 100 m.grms. Ti and 6 m.grms. Ta in another, 50 c.c. 3 per cent H_2O_2 solution were added, and this mixture was dropped rapidly from a separating funnel into a cold mixture of 50 c.c. 3 per cent H_2O_2 and 15 c.c. NH_4OH (0.90); no precipitate formed within fifteen minutes in either case, but a large yellowish white precipitate came out on standing over night at a temperature of about 10° .

G. D., § 7.—100 m.grms. Ti as TiO_3H_4 were dissolved in 10 c.c. 3 per cent H_2O_2 and 2 c.c. HCl (1:12), SO_2 gas passed in to saturation, NH_4OH added till alkaline, the solution allowed to stand three minutes, and then to the mixture a fourth its volume of HCl (1:20) was added; the whole precipitate dissolved. The experiment was repeated, substituting one m.grm. Nb for the 100 m.grms. Ti; the NH_4OH precipitate remained in large part undissolved. The experiment was repeated with a mixture of 50 m.grms. Ti and 2 m.grms. Nb, and with one of 100 m.grms. Ti and 5 m.grms. Nb. In the first case the whole of the NH_4OH precipitate dissolved; and in the second case only a slight one remained, which, when dissolved in H_2SO_4 and treated with Zn and HCl gave no colour, showing the absence of niobium.

G. D., § 8.—See C. E., P. 38, N. 4 in regard to the reduction by Zn and the HgCl_2 test in the cases of titanium and niobium.

G. D., § 9.—To two portions of 7 c.c. H_2SO_4 (1:20), NH_4OH was added till alkaline, and then 7 c.c. $(\text{NH}_4)_2\text{S}$; the mixtures were heated for thirty minutes in a covered casserole, 2 m.grms. W as Na_2WO_4 were added to each, and each was acidified with H_2SO_4 (1:20); to one mixture 3 c.c. 20 per cent FeCl_3 solution was at once added, and both mixtures were shaken and filtered; from that to which no FeCl_3 was added, a small yellowish pink precipitate separated; while in that to which it was added, a decidedly larger orange-yellow precipitate formed; the filtrate was distinctly yellow in both cases.

G. D., § 10.—300 m.grms. W as Na_2WO_4 , 300 m.grms. As as H_3AsO_4 , 100 m.grms. V as Na_3VO_4 , and 50 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$, in separate experiments, were digested with 10 c.c. $(\text{NH}_4)_2\text{S}$, the solution precipitated by H_2SO_4 ; the precipitate, sucked as dry as possible, was transferred to a stoppered Erlenmeyer flask, 20 c.c. HCl (1:20) poured over it, and the mixture heated for twenty minutes on a steam-bath; the flask was connected by means of tubes passing through the stopper with another flask containing a solution of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ strongly alkaline with NaOH, and at the end of the twenty minutes it was removed from the steam-bath and a current of air was drawn through the liquid so as to carry the vapours above it into the $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution; in the cases of the tungsten, arsenic, and vanadium, black precipitates, estimated at 10 m.grms., 5 m.grms., and 15 m.grms. respectively, separated, while in the case of the molybdenum not even a darkening was produced. The acid solution resulting from the action of HCl (1:20) on the WS_3 in this experiment was decanted

* From the *Technology Quarterly*, xvii., No. 3.

through a filter and evaporated to dryness; 10 c.c. HNO_3 (1:20) were added, and the mixture heated; a yellow residue estimated at 10 m.grms. remained, much of which had already separated during the evaporation of the HCl .

The experiment was repeated with 300 m.grms. W , except that HCl (1:12) was used in place of the HCl (1:20); the precipitate of PbS produced seemed to be equal in quantity to that obtained in the preceding test.

300 m.grms. W obtained as WS_3 , as described above, were heated in a flask on a steam-bath for thirty minutes with 20 c.c. HCl (1:20), a current of H_2S being passed continuously through the liquid; the solution was filtered and evaporated to dryness, and HNO_3 was added; there was a yellow residue not much less in quantity than that obtained when no H_2S was passed in.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 3rd, 1906.

Prof. H. E. ARMSTRONG, F.R.S., Past-President, in the Chair.

MESSRS. H. C. IRVING and W. H. GLOVER were formally admitted Fellows of the Society.

The CHAIRMAN gave expression to the sense of loss sustained by the Chemical Society in the death of Professor Pierre Curie, which followed an accident on April 19th. The meeting endorsed the letter of condolence addressed by the President to Mme. Marie Curie, an Honorary and Foreign Member of the Society.

Certificates were read for the first time in favour of MESSRS. ARTHUR JOHN BERRY, 5, University Gardens, Glasgow; WILLIAM JOHN BOWIS, Ph.D., 97, North Road, West Bridgford, Notts; HAROLD CALAM, B.Sc., 71, Cemetery Road, Beeston Hill, Leeds; JOHN DENTON, Horton Villa, Bradford; BERTIE JAMES EATON, Kuala Lumpur, Federated Malay States; ARTHUR BURTON SHEPHERD, B.Sc., 18, Stafford Street, Hull; FRED SMITH, Cliff House, Bruntcliffe, near Leeds; HENRY WREN, 22, Stapleton Hall Road, Stroud Green, N.; GEORGE YOUNG, B.A., B.Sc., 38, Havelock Street, Sheffield.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—ERNEST BARRETT, B.Sc.; RICHARD HENRY BECKETT, B.Sc.; RODERICK HAROLD CAPPER BIRT, B.A.; PERCY GARRETT CHAMBERLAIN, M.A.; EDWIN RODNEY CHRYSTALL; HERBERT REGINALD COOPER; CHARLES DAVIDSON; WILLIAM DICKSON; ROBERT K. DUNCAN; ERNEST FEILMANN, B.Sc., Ph.D.; JAMES LOUIS FOUCAR, B.Sc.; P. BERTRAM FOY; EDWARD GARDNER; RICHARD GODFREY HAMILTON GARVEY; HEM CHANDRA DUTT GUPTA, M.A.; RICHARD JOHN HALL, M.Sc.; JAMES STUART HILLS; WILLIAM TABOR LATTEY; HAMILTON MCCOMBIE, M.A., B.Sc., Ph.D.; RAM CHANDRA MUKERJEE, B.A.; THOMAS JENKINS MURRAY, Ph.D.; EDGAR GALE OLIVER, M.A.; ERNEST ORMEROD, M.Sc., Ph.D.; LAWRENCE GEORGE RICHARDSON; WALTER DALY SCULLER, B.Sc.; DAVID SOMMERVILLE, B.A., M.D.; JAMES FREDERICK SPENCER, M.Sc., Ph.D.; FOSTER SPROXTON, B.Sc.; FRANCIS W. STOREY, B.Sc.; HAROLD AUGUSTINE TEMpany, B.Sc.; GEORGE AUGUSTUS TURNER; JOHN ADAM WATSON; JOHN HENRY WEST; HENRY JOHN WIFFEN; CECIL WYATT-EDGEELL, B.A.

Of the following papers, those marked * were read:—

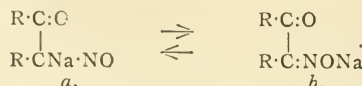
*87. "The Relation between Absorption Spectra and Chemical Constitution. Part V. The Isonitroso-compounds." By EDWARD CHARLES CYRIL BALY, EFFIE GWENDOLINE MARSDEN, and ALFRED WALTER STEWART.

In the previous papers it was shown that when two carbonyl groups are adjacent to one another in a com-

pound, the process of isorropesis is set up between the residual affinities of the oxygen atoms, with the result that an absorption band is produced in the visible blue region of the spectrum, and the compounds are coloured yellow. The principle was extended to the quinones and to the nitrophenols and nitroanilines. A similar condition exists in the isonitroso-compounds, and in the present paper the yellow colour of these substances in alkaline solution is explained. From observations of the absorption spectra of several isonitroso-compounds in neutral and alkaline solution, it is found that the free substances most probably

have the constitution $\begin{array}{c} \text{R}\cdot\text{C}\cdot\text{O} \\ | \\ \text{R}\cdot\text{C}\cdot\text{H}\cdot\text{NO} \end{array}$, but in presence of sodium

hydroxide the hydrogen atom marked with a star is replaced by sodium, and becomes labile, so that a tautomeric process occurs thus—



Isoorropesis then takes place between the $>\text{C}\cdot\text{O}$ and $>\text{C}\cdot\text{N}$ —groups, the tautomeric process being the actuating mechanism. The compounds are therefore yellow in alkaline solution, owing to the presence of an absorption band in the visible blue region of the spectrum, which is due to the isorropesis. There is thus complete analogy between the isonitroso-bodies and quinonemonoxime. An analogous condition is shown to exist in the case of isonitrosocamphor.

DISCUSSION.

Dr. HEWITT drew attention to the way in which Mr. Baly had represented both nitroso- and isonitrosocamphor as equilibrium mixtures, one particular configuration of the molecule being common to both substances. If X be in equilibrium with Y , and Y in turn with Z , then X and Z must also be in equilibrium, and it should be impossible to isolate two different substances, one containing molecules of configurations X and Y , and the other molecules of configurations Y and Z in the case of rapid velocities of transformation.

Dr. LOWRY considered it very improbable that any of the colourless compounds to which Mr. Baly had referred possessed the true nitroso-formula $>\text{CH}\cdot\text{NO}$, since this group usually produces a blue or green coloration. He was surprised that no reference had been made to Beckmann's isoxime-formula, $>\text{C} \begin{array}{c} \text{NH} \\ \diagup \diagdown \\ \text{O} \end{array}$; nitrogen-ethers derived from

the isoximes had been prepared in several cases, and nearly all the colour changes to which Mr. Baly had referred might be explained by the conversion of a coloured oxime into a colourless isoxime and *vice versa* (compare *B.A. Report*, Cambridge, 1904, p. 222). He strongly objected to the application of the term "tautomerism" to substances such as isonitrosocamphor and ethyl acetoacetate; these substances were certainly not "tautomeric" in the sense of Laar's hypothesis, and it would be preferable to describe them in accordance with their actual behaviour as examples of labile or dynamic isomerism.

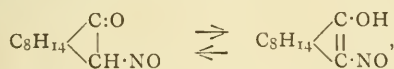
Mr. WM. ROBERTSON asked if Mr. Baly had examined the absorption spectra of the simple oximes. From the physical evidence, such as refractive indices, it would appear that the oximes and their salts were identical in structure, whereas in the case of the isonitroso-compounds a very different condition of affairs obtained. With regard to the isonitrosocamphors, he was of opinion that the stable isonitrosocamphor and its oxygen ethers contain the

grouping $\begin{array}{c} \text{C}\cdot\text{N}\cdot\text{OR} \\ || \\ \text{C}\cdot\text{O} \end{array}$, and that the salts derived from the unstable isomeride are represented by the grouping $\begin{array}{c} \text{C}\cdot\text{NOM} \\ | \\ \text{C}\cdot\text{O} \end{array}$.

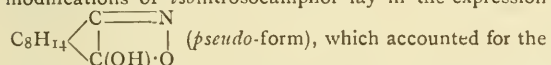
Dr. FORSTER stated that without having had an opportunity of examining the detailed communication, he had some difficulty in dealing with Mr. Baly's references to the views he had from time to time expressed regarding the constitution of *isonitrosocamphor*, but it seemed to him that the most important observation on that point which Mr. Baly and his colleagues had brought forward was the close similarity between the absorption spectra of the stable *isonitrosocamphor* and its O-alkyl ethers. Experiments of a merely chemical nature had made it clear that these ethers and the colourless benzoyl derivative are not

compounds of the type $C_8H_{14} \begin{array}{c} \text{C:N}\cdot\text{OX} \\ | \\ \text{C:O} \end{array}$, and the obvious

inference is that the stable *isonitrosocamphor* likewise belongs to a different class. Nevertheless, he was quite unable to accept the explanation of the authors, who, he understood, represented the stable modification as an equilibrium mixture,—



a system which should surely display some characteristics of a true nitroso-compound. If the stereochemical theory applied to *isonitrosocamphor* had to be abandoned, as to which the speaker was not completely convinced, a more satisfactory explanation of the difference between the two modifications of *isonitrosocamphor* lay in the expression



readiness with which *α*-camphornitrilic acid arose from the colourless derivatives on hydrolysis. As an alternative to

this might be offered the similar formula $C_8H_{14} \begin{array}{c} \text{C}\cdot\text{N}\cdot\text{OH} \\ || \\ \text{C=O} \end{array}$,

but, except in so far as it presented a smoother trans-

position from the unstable form $C_8H_{14} \begin{array}{c} \text{C:N}\cdot\text{OH} \\ | \\ \text{C:O} \end{array}$, it pos-

sessed no great advantage over the *pseudo*-form, although, in the speaker's opinion, certainly preferable to the isoxime constitution.

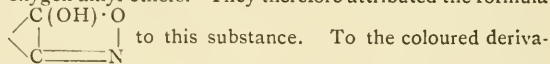
The CHAIRMAN congratulated the meeting on the fact that the paper had been so well discussed, and subjected to the proper criticism to which all papers presented to the Society should be open; it was clearly the general opinion that the conclusions arrived at were unsound. He could not agree that the word "isorropesis" coined by Mr. Baly was a good one, and he protested against its introduction; neither was it necessary, nor did it express the conception which had been brought forward. Apparently it indicated a process in which a state of equipoise or equilibrium was arrived at, to express which no new word was required; in reality, the idea put forward was that the production of absorption bands was due to a wobble or metamorphosis, to change of form, which also could be expressed without a new word. There was a growing practice among scientific workers, whenever a vague new conception was arrived at, to wrap it up in a new word which few could understand. He desired, with whatever authority the Chair gave, to protest in the most emphatic manner possible against the practice. He agreed with previous speakers that nitroso-formulae such as were put forward, could not be used for the colourless compounds under consideration; substances so constituted would be highly coloured. Mr. Baly objected to the interpretation put upon the term isorropesis, and denied that it meant wobble generally; it appeared that he limited it strictly to the wobble involved in the passage from the ketonic to the linked oxygen form of quinone.

Mr. BALY said, in reply to Dr. Hewitt, that the existence of one configuration being common to both processes was no objection. Two possibilities of labile isomerism exist

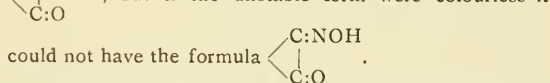
in *isonitrosocamphor*, and one of these they connected with the unstable variety and the other with the stable variety. The existence of a common configuration accounts for the ease with which unstable *isonitrosocamphor* passes over into the stable form.

In reply to Dr. Lowry, he thought that there was no direct evidence that the group $>\text{CH}\cdot\text{NO}$, as suggested, possessed a blue or green colour. The isoxime formula did not seem capable of explaining the absorption curves obtained with the *isonitroso*-compounds. In alkaline solution these bodies all show a strong absorption band in the ultra-violet analogous to ethyl acetoacetate in alkaline solution. Such a band as this does not seem capable of explanation by an equilibrium between the isoxime and oxime form; it must be due to the same type of labile isomerism as is occurring in ethyl acetoacetate.

In reply to Mr. Robertson, the absorption curves show that the stable form of *isonitrosocamphor* in neutral solution possesses the same configuration as Dr. Forster's oxygen alkyl ethers. They therefore attributed the formula



to this substance. To the coloured derivatives of the unstable form they attributed the formula



, but if the unstable form were colourless it could not have the formula $\begin{array}{c} \text{C:NOH} \\ | \\ \text{C:O} \end{array}$.

In reply to Dr. Forster, Mr. BALY apologised for not making himself clear upon the suggestions his colleagues and he brought forward. They were firmly of the opinion that the stable form of *isonitrosocamphor* in neutral solu-

tion was Dr. Forster's own *pseudo*-form $\begin{array}{c} \text{C(OH)}\cdot\text{O} \\ | \\ \text{C=N} \end{array}$, but that in alkaline solution the ring was broken, and that a process of labile isomerism was set up which could be best expressed by saying there was equilibrium between—



the colour in alkaline solution being due to the parallel linking in *a*. Similarly, in the unstable form, their view was that in alkaline solution the labile tautomerism could be best expressed by—

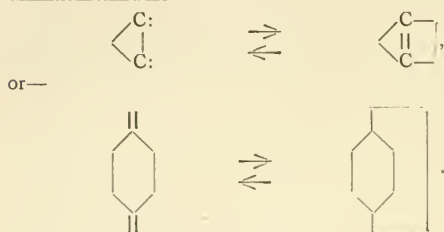


the colour was due to the isorropesis occurring with form *c*. It was difficult to give a formula to the unstable form in neutral solution, as its colour was not absolutely known.

There seemed to be confusion as to the meaning of the term isorropesis, and he would like to state what the process consists in. The simplest case is that of diacetyl, in which compound the residual affinities on the ketonic oxygen atoms disturb one another, with the result that an oscillation is set up which can, perhaps, be graphically expressed—



This process has been named isorropesis, and, in its broadest sense, it means an oscillation between the residual affinities of two or more adjacent atoms or groups of atoms, thus:—



The process might also be looked on as the result of the mutual interference between two systems, each possessing possibilities of labile isomerism, as, for example, the two $\text{CH}_3\cdot\text{CO}$ groups in diacetyl.

*88. "The Residual Affinity of Coumarin as shown by the Formation of Oxonium Salts." By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

Coumarin dissolves much more readily in concentrated hydrochloric acid than in water, and the strongly acid solution, when treated with excess of chloroplatinic acid, yields a yellow crystalline *platinichloride*, $4\text{C}_9\text{H}_6\text{O}_2\cdot\text{H}_2\text{PtCl}_6\cdot 4\text{H}_2\text{O}$, which is dissociated into its generators by water. 6-Aminocoumarin, ethyl-6-aminocoumarin, dimethyl-6-aminocoumarin, and the corresponding quaternary base, like other aromatic amines, all yield platinichlorides, platinibromides, and aurichlorides of the normal type, but the acyl derivatives of 6-aminocoumarin, in which the salt-forming power of the nitrogen atom is largely destroyed, resemble coumarin itself in giving rise to platinichlorides containing a greater proportion of the organic constituent. *Acetyl-6-aminocoumarin platinichloride* has a composition approximating to the formula $4(\text{C}_7\text{H}_5\text{O}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_3)\cdot\text{H}_2\text{PtCl}_6\cdot 4\text{H}_2\text{O}$.

Coumarin dissolves readily in warm fuming hydriodic acid containing free iodine, and from the dark brown solution, dark bronzy-green masses or well-defined needles separate, depending on the concentration; the product, which can be re-crystallised from concentrated hydriodic acid, has the composition of a *hydriodide periodide*, $4\text{C}_9\text{H}_6\text{O}_2\cdot\text{HI}\cdot\text{I}_3$.

The formation of these salt-like additive compounds of coumarin agrees with the results of earlier investigators. Ebert found that this lactone yielded an extremely unstable hydrobromide (*Annalen*, 1884, ccxxvi., 347), whilst W. H. Perkin, sen., described a dichloride and dibromide (*Annalen*, 1871, clviii., 116). Moreover, coumarin exhibits an amphoteric character in combining also with metallic oxides and hydroxides.

DISCUSSION.

Dr. CAIN referred to his paper on "The Constitution of the Ammonium Compounds" (*Mem. Manchester Phil. Soc.*, 1904, xlviii., iii., No. 14), in which he had suggested formulæ for the so-called molecular compounds, similar to those now brought forward by Dr. Morgan. He did not believe in Werner's theory of "Haupt Valenz" and "Neben Valenz" as applied to the ammonium compounds, but was of the opinion that a satisfactory explanation was given by assuming the presence of triad halogen and tetrad oxygen.

Dr. HEWITT remarked that the formation of oxonium salts frequently coincided with the occurrence of another oxygen atom in the molecule, in addition to the salt-forming oxonium oxygen atom; not only in the case of pyrones and coumarins, but also with xanthone and fluorane derivatives. Dr. Cain's formulation of ammonium chloride was open to the objection that it seemed incompatible with the known ionisation of ammonium salts in aqueous solution; a difficulty in no way diminished when one applied corresponding formulæ to the tetra-alkylammonium bases and their salts.

Dr. MORGAN, in reply to a question from Mr. F. H. CARR, stated that they had made many attempts to combine coumarin with metallic salts, such as mercuric oxide, but without success.

89. "Brazilin and Hæmatoxylin. Part VII. Some Derivatives of Brazilin." By PAUL ENGELS and WILLIAM HENRY PERKIN, jun.

Brazilin, $\text{C}_{16}\text{H}_{12}\text{O}_5$, is the colouring matter which is produced when brazilin, $\text{C}_{16}\text{H}_{14}\text{O}_5$, is oxidised in alkaline solution by means of air.

When brazilin is treated with a large excess of methyl sulphate and caustic potash, it is converted into *trimethylbrazilin*, $\text{C}_{16}\text{H}_9(\text{OMe})_3\text{O}_5$, the formula of which was controlled by repeated analysis and the determination of the methoxy-groups by Zeisel's method.

This new orange-yellow, crystalline substance separates from solvents in two modifications, which melt at 160° and 178° respectively. It combines with formic acid, yielding *trimethylbrazilin formic acid*, which crystallises in brilliant garnet-coloured prisms, melts at 143° , and is decomposed into its components by treatment with alcohol. Trimethylbrazilin dissolves in concentrated sulphuric acid, yielding a crimson solution which soon becomes orange, and, when poured into water, deposits a brilliant vermillion, crystalline precipitate which appears to be *trimethylisobrazilin sulphate* (compare J. J. Hummel and A. G. Perkin, *Trans.*, 1882, xli., 9).

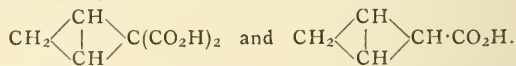
When trimethylbrazilin is left in contact with an alcoholic solution of hydroxylamine, it yields *trimethylbrazilin hydroxylamine*, $\text{C}_{16}\text{H}_9(\text{OMe})_3\text{O}_5\cdot\text{NH}_2\cdot\text{OH}$, an almost colourless, crystalline substance which melts at about 155° with decomposition. This substance dissolves in dilute alkalis with a yellow colour, and is decomposed, on standing, into a neutral substance of melting-point 177° and trimethylbrazilin. It is also decomposed by boiling glacial acetic acid, and the solution, on cooling, deposits crystals of trimethylbrazilin.

The authors wish to reserve these new compounds for further investigation.

90. "The Action of Tribromopropane on the Sodium Derivative of Ethyl Malonate." By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN.

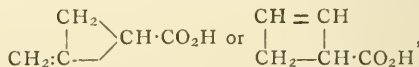
In a previous communication (*Proc.*, 1905, xxi., 256), it was shown that tribromopropane, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, reacts with the sodium derivative of ethyl malonate with formation of an ester $\text{C}_{10}\text{H}_{15}\text{O}_2\text{Br}$.

This ester, when treated with alcoholic potash, yields an acid, $\text{C}_4\text{H}_4(\text{CO}_2\text{H})_2$, which is decomposed on heating, with elimination of carbon dioxide and formation of the corresponding monobasic acid, $\text{C}_4\text{H}_5(\text{CO}_2\text{H})$. Since these two acids do not decolorize bromine, are very slowly oxidised by permanganate, and are not affected by boiling with sodium amalgam, it was suggested that they are probably *dicyclobutane* derivatives of the formulæ—



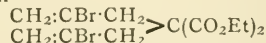
These acids have now been prepared in considerable quantities, and the determination of the magnetic rotation of their esters has proved conclusively that they cannot have the above formulæ, but that they must be unsaturated closed chain compounds.

From a careful investigation of their behaviour, the authors incline to the view that the monobasic acid must be represented by one of the constitutional formulæ—



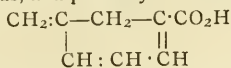
but such formulæ are, obviously, very difficult to establish.

Besides the bromo-ester mentioned above, a second *bromo-ester*, $\text{C}_{13}\text{H}_{18}\text{O}_4\text{Br}_2$, is formed during the action of tribromopropane on the sodium derivative of ethyl malonate; this distils at 191° (11 m.m.), and has either the constitution—

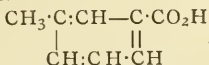


or some constitution closely allied to this.

When digested with alcoholic potash, it yields an acid of melting-point 47° , which closely resembles the *pseudo*-phenylacetic acids, and probably has the constitution—



This interesting acid instantly decolorises permanganate, and when boiled with water or mineral acids, or treated with acetic or hydrobromic acid in the cold, is converted quantitatively by molecular rearrangement into *m*-toluic acid (m. p. 110°)—



For this reason the acid of melting-point 47° has been named *pseudo-m-toluic acid*.

The further investigation of these new compounds is in progress.

91. *Pipitzahoic Acid*." By JAMES MCCONNELL SANDERS.

An investigation of this substance was made by the author at the instance of the Mexican Government, with the object of correcting, if possible, the discrepancies which exist in the literature. Considerable attention is being attracted by this substance owing to its peculiar and valuable properties as a non-toxic purgative. The author describes the method of extraction from the Pipitzahoac root and the properties of the purified acid.

The formulæ of Weld ($\text{C}_{30}\text{H}_{20}\text{O}_6$) and Mylius ($\text{C}_{15}\text{H}_{20}\text{O}_3$) are rejected, the author considering that its composition is best represented by the formula $\text{C}_{10}\text{H}_{14}\text{O}_2$, it being thus isomeric with camphorquinone and similar to, although not identical with, the *isocamphorquinone* discovered by Manasse and formulated by Bredt as $\Delta^1-4(8)$ -terpadienol (*Ber.*, 1902, xxxvi., 3829—3843). Pipitzahoic acid is obtained in golden-yellow scales or orange crystals, and melts at $104-105^{\circ}$; by prolonged heating above its melting-point it loses carbon monoxide and carbon dioxide, giving at first a lemon-yellow sublimate, which melts at $88-89^{\circ}$, and finally a beautifully crystalline, colourless sublimate, which is insoluble in water, but soluble in most organic solvents. This compound, $\text{C}_{11}\text{H}_{14}\text{O}_2$, crystallises from acetone or benzene in glistening prisms melting at 140° , and having an odour of camphor. Its solutions are optically active, a 2 per cent solution in alcohol having $[\alpha]_D = 77.9^{\circ}$ at 25° ; it does not react with hydroxylamine or aniline, but with acetic anhydride forms a compound, $\text{C}_{14}\text{H}_{20}\text{O}_4$, which crystallises from acetone in square plates melting at $114-115^{\circ}$. Pipitzahoic acid is insoluble in water, but soluble in most organic solvents, its solutions being optically inactive. Its violet alkaline solution yields the unchanged substance on acidifying or by extraction with ether. It has a neutral reaction, does not contain methoxy-groups, and does not combine with sodium bisulphite. On fusion with potash, the acid gives methyl hexylene ketone and butyric acid. It forms an *oxime* (m. p. 153.7°), an aniline compound (m. p. $134-135^{\circ}$), and a *dibromide*, which is a yellowish brown, unstable oil. It is not reduced by sulphurous acid, but easily reduced by zinc dust and acetic acid, and when distilled in a current of hydrogen over zinc pumice gives a readily oxidisable liquid which forms optically inactive fluorescent solutions in chloroform and ether. The reduction product itself is isomeric with benzylidenecamphor, $\text{C}_{17}\text{H}_{20}\text{O}$. Pipitzahoic acid seems to behave as a hydroxy-ketone, forming a resinous acetyl compound and a greenish brown *copper* derivative, $(\text{C}_{10}\text{H}_{13}\text{O}_2)_2\text{Cu}$.

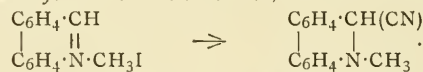
Silk may be dyed an olive-green tint by treating it with a solution of pipitzahoic acid after a preliminary mordanting with copper acetate.

92. "The Constitution of the Hydroxides and Cyanides obtained from Acridine, Methyl-acridine, and Phenanthridine Methiodides." By CHARLES KENNETH TINKLER.

From the results obtained by a study of the ultra-violet absorption spectra of the methiodides, before and after the

addition of caustic soda, it is concluded that the hydroxides produced are carbinols, and are constituted similarly to the hydro-compounds, as in the cases of cotarnine, hydrastinine, and phenylmethylacridol (Dobbie, Lauder, and Tinkler, *Trans.*, 1903, lxxxiii., 598; Dobbie and Tinkler, *Trans.*, 1904, lxxxv., 1005; and 1905, lxxxvii., 269).

The cyanide obtained from phenylacridine methiodide (Hantzsch, *Ber.*, 1899, xxxii., 3109) gives spectra almost identical with those of hydrophenylacridine, thus affording evidence in support of the constitution $\text{C}_6\text{H}_4\text{-}\overset{\text{C}(\text{C}_6\text{H}_5)\text{CN}}{\underset{\text{N}(\text{CH}_3)}{\text{N}}}\text{-C}_6\text{H}_4$ for this substance. A colourless cyanide has been prepared from phenanthridine methiodide. The absorption spectra of the substance agree very closely with those of hydrophenanthridine, and this is only to be explained by adopting the constitution of a *pseudo*-cyanide for this substance,—



93. "The Constitution of Ammonium Amalgam." By MISS ELIZABETH MARY RICH and MORRIS WILLIAM TRAVERS.

The authors have determined the freezing-points of a series of samples of ammonium amalgam, in which the concentration, calculated as grms. of ammonium per 100 grms. of mercury, varied between 0.0094 and 0.507. The value of the "molecular depression" agrees with that obtained by Tammann for solutions of other metals in mercury, leading to the conclusion that ammonium amalgam is a true solution of ammonium in mercury.

94. "Action of Light on Potassium Ferrocyanide." By GLYN WILLIAM ARNOLD FOSTER.

When a neutral or alkaline solution of potassium ferrocyanide is exposed to light, ferric hydrate is slowly precipitated; in presence of alkali sulphide, ferrous sulphide is thrown down.

No precipitation takes place if the solutions are protected from light; the action is therefore entirely photochemical. Potassium ferrocyanide is, in solution, dissociated in the usual manner, into potassium ions and the complex "ferrocyan" ions $[\text{Fe}(\text{CN})_6]^{4-}$; this is in absence of light. On exposure to light, this complex is dissociated into iron ions and cyan ions, and on removing the source of light the complex ferrocyan ion is regenerated. Thus no precipitation of iron can take place in absence of light.

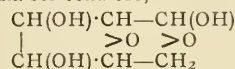
The relations $\text{Fe}:(\text{CN})$ were always below the theoretical 1:6, and this was found to be due to the oxidation of cyanide under the influence of light to cyanate and polymerides. In presence of alkali sulphide the cyanide is almost entirely converted into sulphocyanocompounds.

The source of light used was a mercury vapour lamp of quartz, made by W. C. Heraeus, of Hanau. It was water-cooled, and, using a direct current of 5 to 6 ampères at 240 to 250 volts, gave a very intense light, rich in ultra-violet radiation.

95. "Note on the Constitution of Cellulose." By ARTHUR GEORGE GREEN and ARTHUR GEORGE PERKIN.

It is generally believed that the highest acetyl derivative of cellulose is a tetra-acetate, $\text{C}_6\text{H}_6(\text{OAc})_4\text{O}$.

Green's formula for cellulose,—



(*Zeit. Farb. Text. Ind.*, 1904, iii., 97), contains only three hydroxyl groups, and would therefore yield a *tri*-acetate. As this formula affords a simple and direct explanation of the other reactions of cellulose, a re-examination of the acetate was desirable. Acetyl estimations of the so-called "tetra-acetylcellulose" were therefore made by three different methods:—(a) Perkin's method (*Trans.*, 1905, lxxxvii., 107); (b) alkaline saponification; (c) alkaline

saponification combined with Perkin's method. In each case the numbers obtained agreed closely with those required for the tri-acetate, $C_6H_7(OAc)_3O_2$.

The highest acetate, therefore, like the highest nitrate and benzoate, corresponds with the presence of three hydroxyl groups in the cellulose molecule.

It is suggested that the above expression represents cellulose in its simplest or unpolymerised form, but that fibre cellulose is a colloidal aggregate of a large number of such simple molecules.

96. "Some New Derivatives of Pinene." By FREDERICK PEACOCK LEACH.

When pinene nitroschloride is treated with potassium cyanate in alcohol at $50-60^\circ$, potassium chloride is precipitated, and on pouring the mixture into water a compound, $C_{12}H_{17}O_3N_3$, separates, which after crystallisation from alcohol melts at $238-240^\circ$. The substance is characterised by its great stability, being dissolved by hot concentrated nitric acid without undergoing change.

On reduction with zinc and acetic acid, carbon dioxide and ammonia are eliminated, the compound $C_{11}H_{18}ON_2$ being formed. This melts at 224° , and from its behaviour towards nitrous acid is most probably a ψ -carbamide, giving a well-crystallised nitroso-derivative melting at 159° ; when the latter is reduced, the corresponding ψ -semicarbazide is formed, yielding a benzal- ψ -semicarbazone, $C_{18}H_{23}ON_3$, which melts at 180° . When the compound $C_{12}H_{17}O_3N_3$ is heated with concentrated sulphuric acid, carbon dioxide and ammonia are eliminated, and there is produced a base, $C_{10}H_{18}ON_2$, which crystallises in needles and melts at $123-125^\circ$: $C_{12}H_{17}O_3N_3 + 2H_2O = C_{10}H_{18}ON_2 + 2CO_2 + NH_3$. This compound is amphoteric, and appears to be an amino-oxime; it is obtainable also from pinene nitroschloride by the action of ammonia.

97. "Glutaconic and Aconitic Acids." By SIEGFRIED RUHEMANN.

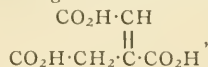
Rogerson and Thorpe show in their papers (*Trans.*, 1905, lxxvii., 1669, 1685; 1906, lxxxix., 631) on glutaconic and aconitic acids that they are unacquainted with several of my publications dealing with these acids, and they misrepresent some of my statements. I feel reluctantly obliged, therefore, to point out their errors.

After having found that ethyl aconitate, on treatment with ammonia, yields citrazinamide (*Ber.*, 1887, xx., 3366), I applied this reaction to the β -alkyl derivatives of ethyl glutaconate, and thus arrived at the β -alkyl substitution products of 2:6-dihydroxypyridine. Thus methyl, ethyl, and benzyl 2:6-dihydroxypyridine have been obtained (*Trans.*, 1893, lxiii., 259, 874), which are oxidised by ferric chloride to yellow substances. Lately, Rogerson and Thorpe have prepared derivatives of 2:6-dihydroxypyridine (*Trans.*, 1905, lxxvii., 1685) which contain alkyl groups in the γ -position and others with the same groups in the β - and γ -positions, and have pointed out that these derivatives react with ferric chloride in a manner different from the β -substituted 2:6-dihydroxypyridines (see Ruhemann, *loc. cit.*), but these chemists appear to be unaware of the fact that I had previously obtained derivatives of 2:6-dihydroxypyridine containing alkyl groups in the γ - and γ - β -positions by the action of ammonia on the products of the union of ethyl phenylpropionate with ethyl malonate or its homologues, and that I have also described their reaction with ferric chloride (*Trans.*, 1899, lxxv., 245). Again, in recording the properties of the $\alpha\alpha'$ -dihydroxypyridines, Rogerson and Thorpe indicate the analogy which exists between these substances and resorcinol, but they seem to have overlooked the fact that I have already recorded this (*Ber.*, 1893, xxvi., 1559).

By the action of ethyl sodiocyanoacetate on ethyl oxaloacetate, Rogerson and Thorpe (*Trans.*, 1906, lxxxix., 640) obtained ethyl α -cyanoaconitate which, under the influence of concentrated sulphuric acid, condenses to ethyl 2:6-dihydroxypyridine-4:5-dicarboxylate. They further show that, on boiling this ester with alkali, it is transformed into citrazinic acid. They state that ethyl

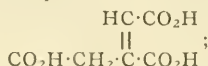
dihydroxycinchomerate had first been prepared by Errera and Perciabosco (*Ber.*, 1901, xxxiv., 3713), but they have overlooked the fact that Ruhemann and Stapleton (*Trans.*, 1900, lxxvii., 250) had obtained it a year before by the action of ammonia on ethyl propenetetracarboxylate, and had described its conversion into citrazinic acid.

I am especially surprised that Rogerson and Thorpe should have misunderstood Ruhemann and Orton's statements concerning the configuration of aconitic acid. They say (p. 634) that we assigned to this acid the configuration—



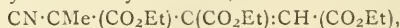
"on account of its formation from citrazinamide by the action of caustic potash at 150° , and also owing to the formation of citrazinamide by the action of ammonia on ethyl aconitate." As a matter of fact, the former reaction has never been advanced as a proof of the fumaroid structure. This was mainly derived from a careful study of the transformations of citrazinamide. I need not here enter into the arguments which support this view, because they are fully discussed in the paper to which Rogerson and Thorpe refer (Ruhemann and Orton, *Ber.*, 1894, xxvii., 3449).

The research described in this paper points to the existence of the other possible stereoisomeride,—

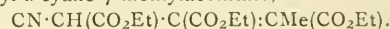


it was suggested only that the latter is "probably" identical with Baeyer's aceconitic acid (*Annalen*, 1865, cxxv., 306), but not put forward as our definite opinion, as Rogerson and Thorpe seem to imagine (*Trans.*, 1906, lxxxix., 634).

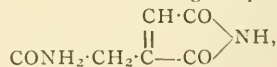
Rogerson and Thorpe arrive at a different conclusion as to the formula of aconitic acid by assigning to it a symmetrical structure, similar to that which they give to glutaconic acid. They support this view by demonstrating the formation of the same methylaconitic acid from both ethyl α -cyano- α -methylaconitate,—



and ethyl α -cyano- γ -methylaconitate,—



The same criticism which Feist and Beyer (*Annalen*, 1906, cccxlv., 117), who succeeded in proving the existence of both stereoisomeric β -methylglutaconic acids, offer to Rogerson and Thorpe's symmetrical structure of glutaconic acid applies also to the symmetrical structure of aconitic acid. Without entering into further discussion of the conclusions at which these chemists arrive, I will only point out that if their view were correct, the action of ammonia on ethyl aconitate may be expected to yield, besides citrazinamide, a five-membered ring compound,—



but the formation of this compound does not take place.

Research Fund.

A Meeting of the Research Fund Committee will be held in June next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before Monday, June 4th, 1906.

Those Fellows who received grants in June, 1905, or whose grants, allotted in June of previous years, have not been closed, are reminded that reports must be in the hands of the Hon. Secretaries not later than Friday, June 1st, 1906.

Cleve Memorial Lecture.

The Cleve Memorial Lecture will be delivered by Prof. T. E. Thorpe, C.B., F.R.S., on Thursday, June 21st, 1906, at 8.30 p.m., before the business of the Ordinary Meeting.

PHYSICAL SOCIETY.

Ordinary Meeting, May 11th, 1906.

Dr. C. CHREE, F.R.S., Vice-President, in the Chair.

A PAPER ON "*The Dead Points of a Galvanometer Needle for Transient Currents*," was read by Mr. A. RUSSELL.

When many types of needle galvanometer are connected with a condenser and a battery in the ordinary manner by a charge and discharge key the following phenomena can easily be observed:—When the needle is initially at right angles to the axis of the galvanometer-coil, and the spot of light is in the centre, X, of the scale, the throws on charge and discharge are equal. If the controlling magnet be turned through a small angle, or if the suspending fibre be twisted slightly so that the spot of light is not in the centre of the scale initially, the throws on charge and discharge are not equal. The algebraic difference between them, however, is constant. Hence, for an initial position P_1 of the spot of light there is no throw on charge, and similarly for another initial position P_2 there is no throw on discharge. These points the author calls the dead points. If the resistance of the charging and discharging circuits are the same, $XP_1 = XP_2$. In this case the distance P_1P_2 varies directly as the resistance of the charging circuit, and inversely as the applied voltage. If the initial position of the spot of light be outside of P_1P_2 , the throws on charge and discharge are in the same direction. The author shows that these effects can be explained with considerable accuracy by supposing that the magnetism of the needle consists of two parts, one permanent and the other proportional to the magnetising force. As far back as 1868 Lord Rayleigh showed that this supposition is sufficient to explain the permanent deflexion produced by an alternating current passing through the galvanometer-coil. In a paper also, in 1883, he pointed out that a galvanometer is a very imperfect instrument for indicating whether the integral sum of the transient currents through it is zero or not, and he also mentioned the limitations this imposes on Maxwell's method of comparing mutual inductances. The author finds that it is easy to arrange with a low-resistance galvanometer so that a, relatively speaking, gigantic charge can be passed through the coil without producing any throw at all. He also finds that all the galvanometers he has tested, whether needle or moving coil, will produce throws when certain transient currents pass through them, even although the integral value of these currents is zero. It also appears that the effective internal resistance of ordinary condensers is appreciable in certain cases. These results are of importance in connection with several of the customary methods of testing.

Mr. W. DUDELL expressed his interest in the paper, and remarked that the phenomena described were of importance in the measurement of capacity. He suggested that since the R term in the paper included all the i^2R losses, part of it might arise from eddy-currents in the condenser. The condenser shown by the author was constructed by winding together very long strips of tin-foil, and the resistance should therefore appear high if it was true resistance; perhaps Mr. Russell could tell him the value of the resistance of the condenser shown.

Prof. H. A. WILSON, referring to the effective internal resistance of a condenser, pointed out that if there was dielectric hysteresis there must be a loss of energy, which no doubt amounted to a resistance as determined by the author.

Mr. ROLLO APPELYARD asked if it was necessary to assume that R was a resistance. It might be a physical constant of the condenser of another kind.

Mr. A. CAMPBELL said that the effects mentioned by Mr. Russell often gave trouble in actual testing-work. Some years ago he found that in testing standard air-condensers by Maxwell's method, an ordinary needle galvanometer gave erroneous results unless its needle was exactly in the symmetrical position. A moving coil-galvanometer, however, gave satisfactory results.

The AUTHOR, in reply to Prof. Wilson, stated that dielectric hysteresis had probably some connection with the internal resistance of the condenser, but the effect was small. The energy radiated into space was also small. Mr. Duddell's suggestion of eddy-currents might clear up any lack of uniformity in results obtained with very rapid oscillatory discharges. The author also showed how the resistance of a condenser could be measured in a minute or two by his method. The resistance of the actual condenser used in the experiments was found to be about 9 ohms.

Prof. H. A. WILSON exhibited a Lippmann Capillary Dynamo and Electromotor from the George the Third Museum of King's College.

Mr. W. DUDELL exhibited some Mechanical and Electrical Phenomena occurring in the Telephonic Transmission of Speech.

The apparatus is intended to demonstrate as curves on a screen the simultaneous movement of the microphone transmitter-diaphragm, the current flowing into the telephone line, the current received at the far end of the line, and the movement of the receiver-diaphragm when sounds or speech are being transmitted. The similarity of and the difference between these four curves can be examined by the aid of the apparatus, and the distortion and attenuation produced by the resistance, capacity, and self-induction of the line can be demonstrated, as well as the distortions produced by the diaphragms of transmitter and receiver. The characteristic shapes of the curves corresponding to the different vowel-sounds and their dependence on the pitch on which they are sung can also be exhibited.

CITY AND GUILDS OF LONDON INSTITUTE.

A GENERAL Meeting of Old Students was held at the Technical College, Finsbury, on Tuesday evening, May 8th, 1906, at which Sir OWEN ROBERTS, M.A., D.C.L., J.P., took the chair. About 120 old students attended this meeting to discuss the proposal to form an Old Students' Association. In a short opening speech Sir Owen Roberts expressed his approval of such Associations, and said that it gave him great pleasure to preside at the organisation meeting of such a one as this promises to be. Among other things he expressed his sympathy with its objects, and promised his hearty co-operation.

The CHAIRMAN then called on Mr. P. V. McMAHON, M.Inst.C.E., M.I.E.E., &c., to propose the following resolution:—"That an Old Students' Association be formed for—

- (a) The promotion of social intercourse;
- (b) The advancement of the interests of the Technical College and of past Students;
- (c) Mutual help."

This was seconded by Mr. T. J. UNDERHILL, Chief Inspector of Victualling Stores to H.M. Navy, and carried unanimously.

Mr. J. L. BAKER, F.I.C., Hon. Secretary of the London Section of the Society of Chemical Industry, then proposed, and Mr. C. E. HOLLAND, M.A., seconded, the next resolution, which was:—"That the draft scheme of the Organising Committee be provisionally adopted, and that it be an instruction to the Council to draw up a Constitution and By-laws, and to submit them to a General Meeting."

The following draft scheme was proposed:—

The Officers of the Association shall be a President, to be chosen annually in turn from each Department; Vice-Presidents, not to exceed six, of whom at least one shall be chosen from each Department; and three Secretaries, chosen by the Members of the Association.

Each Department shall elect a Standing Committee of nine Members to deal with purely departmental matters (e.g., the registration of members seeking or offering employment) who shall nominate five (of whom at least

one shall be an evening student) of their number to serve with the Officers as a General Council.

It is suggested that the appointment of a Standing Social Committee, and a Consulting Committee composed of Members of responsible position, to act with the Principal and Professors of the College, in advising, arbitrating, and helping Old Students in difficulties, should occupy the early attention of the Council.

All Past Students of the College shall be eligible as Members or Associates, but no one shall remain an Associate who has left the College more than five years. Past Members of the Staff, and Members of the Governing Body of the Institute, shall be eligible for full membership, and all present members of the staff shall be Honorary Members.

The subscription shall be 10s. 6d. per annum for Members, and 5s. for Associates.

After much discussion the resolution was passed with the following amendments:—(1) That there should be one class of Members only; (2) that the subscription be 5s. for London Members and 2s. 6d. for Country Members.

During the discussion Sir OWEN ROBERTS said that he felt sure that various City Companies would give financial support to the movement, and that he would put the matter before the Court of the Clothworkers' Company, which he represented.

The business of electing the Officers of the Association was then proceeded with, and Mr. A. H. MACCALLUM proposed, and Mr. R. G. PELLY, A.I.C., seconded, Dr. M. O. Forster, D.Sc., F.R.S., &c., as President of the Association. Dr. Forster's name was received with much enthusiasm, and he was unanimously elected.

The following officers were then proposed by Mr. MACCALLUM and seconded by Mr. PELLY, and were duly elected:—

Vice-Presidents—Sir Owen Roberts, M.A., D.C.L., J.P.; Prof. J. Perry, D.Sc., F.R.S., &c. *Mechanical*—C. G. Redfern. *Electrical*—P. V. McMahon, M.Inst.C.E., M.I.E.E., M.I.Mech.E. *Chemical*—H. D. Richmond, F.I.C.

Treasurer—Prof. W. E. Dalby, M.A., B.Sc., M.Inst.C.E., &c.

Secretaries.—*Mechanical*—S. E. Gritton. *Electrical*—E. W. Moss. *Chemical*—J. W. Brooker, A.I.C.

Five Members from each Department to serve on the Council:—

Electrical—A. C. Eborall, M.I.E.E.; H. W. Handcock, M.I.E.E.; H. B. Atkinson, M.I.E.E.; F. H. Halder, M.I.E.E.

Mechanical—A. H. MacCallum; H. N. Waynforth, A.M.I.M.E.; B. Chatterton; M. de Ville, A.M.I.M.E.

Chemical—J. L. Baker, F.I.C.; G. T. Morgan, D.Sc., F.I.C.; M. Priest, F.I.C.; W. J. Pope, F.R.S., F.I.C.; A. R. Ling, F.I.C.

The newly-elected PRESIDENT then proposed a vote of thanks to Sir Owen Roberts for kindly acting as Chairman. Prof. S. P. THOMPSON, D.Sc., F.R.S., &c., in seconding the vote, which was very heartily accorded, gave a short history of the movement, and said how pleased he was to see the Association thus formed.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, May 29, at 5 o'clock, Colonel V. Balck begins a course of two lectures at the Royal Institution on "Northern Winter Sports—Sweden and its People"; and on Saturday, June 2, at 3 o'clock, Professor W. Macneile Dixon delivers a lecture on "The Origins of Poetry." The Friday Evening Discourse on June 1 will be delivered by Professor H. Moissan on "L'Ebullition des Métaux," and on June 8 by Professor Sir James Dewar on "Studies on Charcoal and Liquid Air."

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Reviving Faded (Black) Ink.—(Reply to S. G. W. Mann).—The writer once revived some very ancient writing in ink that had been black by steeping the parchment document in a cold weak aqueous infusion of nut galls. For safety, only a small portion should be operated on at first.—SCRIBE.

MEETINGS FOR THE WEEK.

MONDAY, 28th—Society of Arts, 8. (Cantor Lectures). "Heraldry in relation to the Applied Arts," by George W. Eve.

TUESDAY, 29th.—Royal Institution, 5. "Northern Winter Sports," by Col. V. Balck.

— Society of Arts, 8. "Glass Cutting," by Harry Powell.

THURSDAY, 31st.—Royal Institution, 5. "Man and the Glacial Period," by Prof. W. J. Sollas, F.R.S.

FRIDAY, June 1st—Royal Institution, 9. "L'Ebullition des Métaux," by Prof. H. Moissan, D.Sc., &c.

SATURDAY, 2nd.—Royal Institution, 3. "The Origins of Poetry," by Prof. W. Macneile Dixon, M.A., &c.

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Mdme. CURIE'S Thesis

ON

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THE CHEMICAL NEWS.

VOL. XCIII., No. 2427.

ON THE DISTRIBUTION OF RADIUM IN THE EARTH'S CRUST, AND ON THE EARTH'S INTERNAL HEAT.*

By the Hon. R. J. STRUTT, F.R.S., Fellow of Trinity College, Cambridge.

(Concluded from p. 237).

4. Results for Igneous Rocks.

THE results for igneous rocks will now be given in tabular form and in order of radium content. (See Table II.).

It will be observed that, in general, rocks like granite, with a high percentage of silica, are richer in radium than basic rocks. The rule, however, is by no means invariable.

Uranium ores occur in several of the rocks examined; thus the granites Nos. 2 and 6 occur near the pitchblende-bearing veins which were worked at Wheal Trenwith, St. Ives. The Norwegian syenite rocks, Nos. 3, 8, and 15, also contain local deposits of uranium-bearing minerals. These various rocks are fairly rich in radium, but do not stand in a class by themselves.

Thus the concentration of radium in such deposits is extremely local, and cannot appreciably disturb any general conclusions as to the total amount of radium in the earth's crust.

Confirmatory of this conclusion is the fact that the temperature gradient at Wheal Trenwith, St. Ives, is quite normal (see Prestwich, "Controverted Questions in Geology," p. 216). Considerable quantities of pitchblende occur in this mine, but they are evidently insufficient to cause appreciable disturbance in the distribution of temperature.

5. Meteorites.

Determinations have been made on one stony meteorite, on three samples of meteoric iron, and on a sample of native iron from Ovivak, Disco Island, Greenland (see Table III.). The quantities available have been various, and are entered on the list of results. Where the radium is entered as 0, it is to be understood that no leak was obtained which could clearly be distinguished from that normal to the electroscope.

It will be observed that the stony meteorite contains about as much radium as those basic terrestrial rocks which it resembles in general composition. No evidence was obtained of the presence of radium in iron meteorites. The Greenland iron contains a little radium. This was probably present in the siliceous material contained in this iron, which had been filtered off, decomposed by fusion, and added to the main solution.

6. The Earth's Internal Heat.

If q be the mean mass of radium per c.c. in the earth, h the heat production of radium per gram. per second, then the total heat production must be, per second,—

$$q \cdot h \cdot \frac{4}{3}\pi R^3.$$

If k be the thermal conductivity of the surface rocks, then the total outflow of heat per second will be—

$$4\pi R^2 k \cdot \left(\frac{d\theta}{dr}\right)_R;$$

where $\left(\frac{d\theta}{dr}\right)_R$ is the temperature gradient near the surface, as observed experimentally.

If the earth is in a thermally steady state, then these expressions will be equal, *i.e.*,—

$$4\pi R^2 k \left(\frac{d\theta}{dr}\right)_R = \frac{4}{3}\pi R^3 \cdot q \cdot h,$$

or—

$$q = \frac{3k}{hR} \left(\frac{d\theta}{dr}\right)_R.$$

For k I take the value 0.0041 (see Prestwich, *loc. cit.*). For the temperature gradient 1°F. in 42.4 feet (*loc. cit.*), or, in C.G.S. system, 4.3×10^{-4} .

One gram. of radium bromide produces 100 calories per hour. This gives for h the value 4.75×10^{-2} .

R , the earth's radius = 6.38×10^8 . Thus—

$$q = \frac{3 \times 4.1 \times 10^{-3} \times 4.3 \times 10^{-4}}{4.75 \times 10^{-2} \times 6.38 \times 10^8} = 1.75 \times 10^{-13}.$$

If therefore we assume the earth to be in thermal equilibrium, then, even if the whole of the internal heat is due to radium, the mean quantity per c.c. cannot much exceed 1.75×10^{-13} gram. per c.c., always supposing that the heat production of radium is not materially diminished under the conditions prevailing inside the earth.

Rutherford (*loc. cit.*), taking somewhat different values for the constants involved, gave the value 2.6×10^{-13} radium bromide, equivalent to 1.52×10^{-13} gram. radium per c.c.

It will be observed that all the igneous rocks examined, without exception, contain far more radium per c.c. than this. The poorest of all, Greenland basalt, contains more than ten times as much; an average rock something like fifty or sixty times.

The question must be faced:—Why has not the earth a temperature gradient far larger than that observed?

The calculation given above assumes:—

1. That the earth is in thermal equilibrium, *i.e.*, that the amount of heat which escapes per second is equal to the supply produced in that time.
2. That no other source of internal heat than radium exists.
3. That a gram. of radium produces as much heat inside the earth as at the surface.

As to the first assumption, to suppose that the earth is cooling only aggravates the difficulty. To assume that it is getting hotter is an explanation not likely to be regarded with favour. I have not yet considered it quantitatively.

As to the second assumption, there can be little doubt that a quantity of uranium proportional to the amount of radium, exists in the rocks. (Too little to be detected in the ordinary course of analysis). Moreover, a trace of thorium is not improbably present. These sources of heat are not likely to be important, as compared with radium. There is, too, the possibility of the radio-activity of ordinary materials. If, however, a heating effect from them is assumed, of the order of magnitude to be expected from the ionisation they give, a temperature gradient would result something like 1000 times larger than that observed. I think this argument is conclusive against the theory that they have a genuine radio-activity of this order of magnitude. (See *Nature*, December 21, 1905).

There remains the third assumption, stated above. This cannot be passed over so lightly as the others, but will be more conveniently discussed later. I shall suppose for the moment that it is justified, and that the earth cannot contain more on the average than 1.75×10^{-13} gram. of radium per c.c.

For surface rocks the experiments show that 5×10^{-12} gram. per c.c. is a representative value. This is, if anything, an understatement. Thus not more than about 1/30 of the earth's volume can consist of material similar to that encountered on the surface. This gives a depth of about 45 miles for the rocky crust, assuming the total absence of radio-active material within.

* A Paper read before the Royal Society, April 5, 1906.

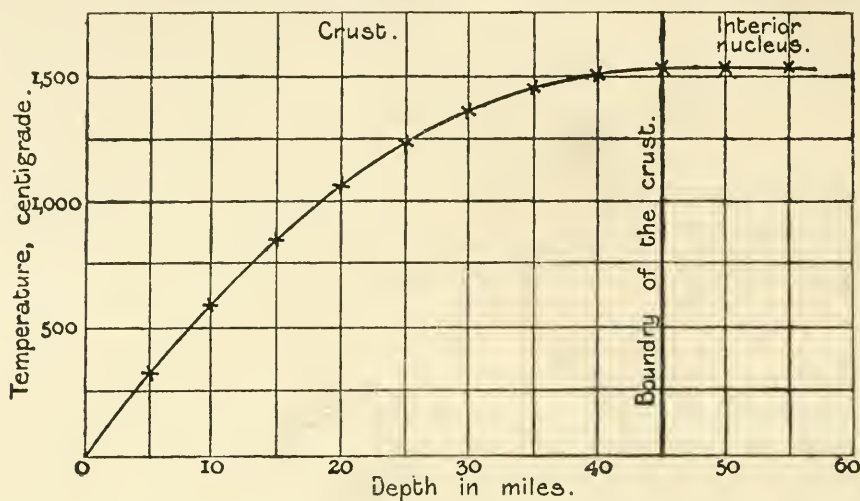


FIG. 2.—Calculated Distribution of Temperature in the Earth's Interior.

TABLE II.

No.	Name of rock.	Locality.	Density.	Radium per grm., in grms.	Radium per c.c., in grms.
1.	Granite	Rhodesia	2.63	9.56×10^{-12}	25.2×10^{-12}
2.	Granite	Lamorna Quarry, Cornwall	2.62	9.35 "	24.5 "
3.	Zircon syenite	Brevig, Norway	2.74	9.30 "	25.5 "
4.	Granite	Rosemorran, Cornwall (?)	2.62	8.43 "	22.1 "
5.	Granite	Cape of Good Hope	2.67	7.15 "	19.1 "
6.	Granite	Knill's Monument, near Carbis Bay, St. Ives, Cornwall	2.61	6.90 "	18.0 "
7.	Granite	Shap Fell, Westmoreland	2.65	6.63 "	17.6 "
8.	Elæolite syenite	Laurdal, Norway	2.70	4.88 "	13.2 "
9.	Granite	Haytor, Devonshire?	2.61	3.69 "	9.64 "
10.	Blue ground	Kimberley	3.06	3.37 "	10.3 "
11.	Leucite basanite	Mt. Somma, Vesuvius	2.72	3.33 "	9.07 "
12.	Hornblende granite.. ..	Assouan, Egypt	2.64	2.45 "	6.47 "
13.	Pitchstone.. ..	Isle of Eigg	2.41	2.06 "	4.97 "
14.	Hornblende diorite	Schriesheim, near Heidelberg	2.89	1.98 "	5.73 "
15.	Augite syenite	Laurvig, Norway	2.73	1.86 "	5.07 "
16.	Peridotite	Isle of Rum	3.15	1.37 "	4.32 "
17.	Olivine basalt	Talisker Bay, Skye	2.89	1.32 "	3.82 "
18.	Olivine euchrite	Isle of Rum	2.97	1.28 "	3.80 "
19.	Basalt	Victoria Falls	2.75	1.26 "	3.46 "
20.	Hornblende granite.. ..	Mt. Sorrel, Leicestershire	2.71	1.25 "	3.38 "
21.	Dolerite	Isle of Canna	2.95	1.24 "	3.65 "
22.	Greenstone	Carrick Dú, St. Ives	2.99	1.14 "	3.41 "
23.	Basalt	Giant's Causeway, Antrim	2.80	1.03 "	2.89 "
24.	Serpentine.. ..	Cadgwith, Lizard	2.60	1.00 "	2.60 "
25.	Granite	Isle of Rum	2.61	0.723 "	1.89 "
26.	Olivine rock	Isle of Rum	3.22	0.676 "	2.18 "
27.	Dunite	L. Scaivig	3.34	0.664 "	2.22 "
28.	Basalt	Ovifak, Disco Island, Greenland.. ..	3.01	0.613 "	1.84 "

TABLE III.

Material.	Locality.	Quantity taken.	Radium per grm.
Stony meteorite	Dhurmsala	50 grms.	1.12×10^{-12}
Meteoric iron.. ..	Thunda.. ..	60 "	0
Meteoric iron.. ..	Augusta Co., Virginia	32 "	0
Meteoric iron.. ..	Santa Catarina	50 "	0
Native iron	Disco Island, Greenland	200 "	0.424×10^{-12}

I shall next consider the distribution of temperature in a crust of this thickness. The curvature of so thin a crust is relatively small, and may, without appreciable sacrifice of accuracy, be disregarded. Let x be the depth at any

point, measured from the outer surface, q the quantity of radium per c.c., h the heat developed in one second by 1 grm. of radium, θ the temperature at the depth x , and k the thermal conductivity.

Then the equation of conduction is—

$$\frac{d^2\theta}{dx^2} = -\frac{qh}{k},$$

which gives by integration—

$$\theta = -\frac{qh}{2k}(x^2 + ax + b);$$

where a and b are constants.

If the surface of the earth be assumed to be at 0°C ., then $\theta = 0$ when $x = 0$.

If l be the thickness of the crust, $d\theta/dx = 0$, when $x = l$. This is clear, since the temperature must be a maximum at the inner boundary of the crust. The interior core, free from radium, must be at a uniform temperature throughout.

Substituting these values, we get—

$$b = 0 \text{ and } a = 2l.$$

Hence—

$$\theta = \frac{qh^2}{2k}(2l - x).$$

Substituting the numerical values adopted in this paper,—

$$\theta = \frac{5 \times 10^{-12} \times 4.75 \times 10^{-7} \times (2 \times 7.25 \times 10^8 - x)}{2 \times 4.1 \times 10^{-3}} = 2.90 \times 10^{-11}x (1.45 \times 10^7 - x).$$

The curve appended shows this distribution of temperature graphically.

The maximum temperature at the bottom of the crust will be where $x = 7.25 \times 10^8$. This gives $\theta = 2.90 \times 10^{-11} \times (7.25)^2 \times 10^{12} = 1530^\circ$, a temperature considerably below the melting-point of platinum.

(NOTE.—No doubt the assumption of constant conductivity at all temperatures is an unsatisfactory feature in this calculation. It is difficult to know what other assumption to make, however. Some experiments of Lord Kelvin and Mr. Erskine Murray (*Proc. Roy. Soc.*, vol. lviii., p. 162) seem to indicate a diminution of conductivity with temperature. On the other hand, Mr. C. H. Lees found the thermal conductivity of window glass to increase with temperature, and at high temperatures rock magmas must approach the quality of glass; indeed, they sometimes even retain that quality on cooling (obsidian and pitch-stone). The mean thermal conductivity of rock cannot be much more than that assumed, for otherwise the internal temperature would not be high enough to produce volcanic phenomena).

This result has been obtained on the provisional assumption that the heat production of radium is the same throughout the earth's crust as under surface conditions. In justification of this, a paper by Mr. W. Makower may be referred to (*Proc. Roy. Soc.*, A, vol. lxxvii., p. 241). The activity of radium emanation and its products are shown to be substantially the same at temperatures of 1200° as at the ordinary temperature, though evidence was obtained of a slight change of activity in one of the products. Thus there is no reason at present to think that notable change of activity sets in before 1500° is reached. I wish to express myself with some reserve on this subject. Further experiments might conceivably show a rapid loss of activity as this temperature was approached. In that case the conclusions here drawn as to the earth's internal condition would require modification.

I was inclined at first to think it incredible that the earth's crust could have so small a thickness as 45 miles, and was therefore much interested to hear that Professor Milne had come to a substantially identical conclusion, from a study of the velocity of propagation of earthquakes through the earth's interior (Bakerian Lecture, 1906). He gives 30 miles as the thickness. This is quite consistent with my data, if rocks like granite, rich in radium, are assumed to be somewhat more abundant than I have supposed, in taking the value 5×10^{-12} gm. radium per c.c. as representative,

Professor Milne expresses the opinion that a fairly abrupt transition occurs at a depth of 30 miles, and that the material below that depth is fairly uniform throughout the globe. This is entirely in agreement with the view put forward above with regard to the earth's interior.

The chemical nature of the interior is a difficult problem. It can scarcely consist mainly of iron, as has been very commonly supposed, from the analogy of meteorites. Meteoric iron is remarkably free from radium, as shown above, and in this respect answers the requirements well enough. But if the stony exterior of the earth is but a small fraction of the whole volume, it cannot have much influence on the mean density, which should be nearly equal to that of the core. The density of the earth (5.5), is much less than the density of iron (7.7).

7. Internal Heat of the Moon.

The data of this paper have an interesting application to the moon. What we can observe of the moon's surface suggests that it consists of rock like that on the earth. The moon is believed to have originally separated from the earth's surface, and should therefore consist of the same material as the latter. Moreover, the density of the moon (3.5) does not differ much from that of rock. It seems reasonable to conclude from these facts that the moon consists almost entirely of rock similar to that of the earth's crust.

On this view, the temperature gradient of the moon should be very great in comparison with that of the earth. The material of the moon is taken to be some thirty times richer in radium than the (mean) material of the earth. Her volume is about one-fiftieth that of the earth. Thus the total heat production in the moon would be about half of that in the earth. This heat has to flow out through about one-sixteenth the area of the earth surface. Thus the temperature gradient at the moon's surface should be eight times greater than at the earth's.

In addition to this, gravity is very much less on the moon. We may conclude that the conditions which prevail there are far more favourable to manifestation of the internal heat by volcanic upheaval. This fully explains why volcanic features are so much more prominent on the moon than on the earth.

It has generally been supposed that the lunar craters are extinct. But that view seems to rest chiefly on an *à priori* conviction that the moon has no internal heat. As Professor W. H. Pickering has pointed out, all those observers who have made a special study of the moon have believed in the reality of changes occurring there (*Nature*, January 5, 1905).

8. Summary of Conclusions.

1. Radium can easily be detected in all igneous rocks. Granites, as a rule, contain most radium, basic rocks the least.
 2. This distribution of radium is uniform enough to enable a fair estimate to be made of the total quantity in each mile of depth of the crust.
 3. The result indicates that the crust cannot be much more than 45 miles deep, for otherwise the outflow of heat would be greater than is observed to be the case. The interior must consist of some totally different material. This agrees entirely with Professor Milne's conclusion drawn from a study of the velocity of propagation of earthquake shocks through the interior.
 4. The moon probably consists for the most part of rock, and if so, its internal temperature must be far greater than that of the earth. This explains the great development of volcanoes on the moon.
 5. Iron meteorites contain little, if any, radium. Stony ones contain about as much as the terrestrial rocks which they resemble.
- In conclusion, I must thank Mr. A. Harker, Mr. Clement Reid, and Mr. A. Hutchinson for their kindness in providing me with various specimens of rock, and for information on geological matters.

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

PART II.—ANALYSIS OF THE TUNGSTEN GROUP.

By ARTHUR A. NOYES.

(Continued from p. 240).

Confirmatory Experiments and References (continued).

P. 31, N. 2.—One m.grm. Sb as Sb_2O_3 , 1 m.grm. Cu as CuSO_4 , and 1 m.grm. Bi as $\text{Bi}(\text{NO}_3)_3$ were separately dissolved in 5 c.c. 48 per cent HF, and 40 c.c. water, and H_2S was passed into the solution in a covered dish for fifteen minutes; a considerable precipitate formed in each solution, which was orange-coloured in the first case and black in the other cases.

100 m.grms. Bi as $\text{Bi}(\text{NO}_3)_3$ were dissolved in 5 c.c. 48 per cent HF and 40 c.c. water, the solution filtered, the filtrate saturated with H_2S , the precipitate filtered out, the filtrate evaporated with H_2SO_4 , and NH_4OH added; no precipitate resulted.

100 m.grms. Se as SeO_2 and 100 m.grms. Te as TeO_2 were separately dissolved in 3 c.c. 48 per cent HF and 24 c.c. water, and H_2S passed into saturation; a large precipitate immediately separated. This was filtered off, the filtrate evaporated to dryness, HCl (1.02) added, and H_2S passed first into the solution in the cold and then into it at a nearly boiling temperature; no more precipitate separated in either case.

500 m.grms. As_2O_3 were treated with HNO_3 (1.42), and the solution evaporated just to dryness; then 3 c.c. 48 per cent HF and 24 c.c. water were added, and H_2S passed in; a precipitate formed only after several minutes, and this continued to increase for an hour. It was then filtered out, and H_2S passed into the filtrate; a large precipitate again resulted.

100 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$ and 4 m.grms. W as Na_2WO_3 were dissolved in 5 c.c. 48 per cent HF and 40 c.c. water, and H_2S was passed into the cold solution for thirty minutes. The precipitate was treated by P. 43; there was only a scarcely noticeable yellow residue (of H_2WO_4) after the evaporation with H_2SO_4 . The filtrate from the H_2S precipitate was treated by P. 33, 35, 39, 41, omitting the HCl treatment, and P. 43; a fairly large yellow residue (of H_2WO_4) resulted.

A mixture of 400 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$, 8 m.grms. Sn, and 8 m.grms. W in HF solution was dissolved in 5 c.c. 48 per cent HF and 40 c.c. water; 2 c.c. H_2SO_4 (1.84) were added, and H_2S was passed for thirty minutes into the cold solution; the precipitate was treated by P. 41, 42, and 43, and the filtrate by the usual complete procedure; the HgCl_2 test obtained by treating the precipitate was only about one-fourth as large as that obtained by treating the filtrate; no tungstic acid separated in the analysis of the precipitate, while a large quantity was obtained in that of the filtrate upon treating the ignited sulphide with HNO_3 and H_2SO_4 .

300 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$ were dissolved in 5 c.c. 48 per cent HF and 40 c.c. water, H_2S passed into the cold solution for thirty minutes, and the mixture filtered; a large black precipitate resulted, and the filtrate became very turbid on short standing. The filtrate was placed on a steam-bath and H_2S passed into the hot solution for thirty minutes more, and filtered; a much smaller precipitate was obtained than before. This last precipitate was treated with HNO_3 (1.20), and the solution was filtered; the residue was ignited, and the filtrate from it evaporated, the two residues united, heated to a low red heat, and weighed; 39 m.grms. of MoO_3 corresponding to 26 m.grms. Mo were obtained. The filtrate from the second H_2S precipitate was evaporated, and the residue ignited and weighed; 45 m.grms. MoO_3 corresponding to 30 m.grms. Mo were obtained. This shows that of the

300 m.grms present only 56 m.grms. remained unprecipitated after the first thirty minutes' treatment with H_2S in the cold.

The last experiment was repeated, except that 3 c.c. H_2SO_4 were added to the HF solution before passing in H_2S , and except that no quantitative determinations were made, the two precipitates obtained were of nearly the same size as before.

500 m.grms. Sn as metal were treated with HNO_3 (1.42), and the latter evaporated off; the residue was dissolved in 5 c.c. 48 per cent HF and 40 c.c. water, and H_2S passed into the cold solution for over an hour; no precipitate appeared.

500 m.grms. W as Na_2WO_3 were dissolved in 3 c.c. HF and 24 c.c. water, and the cold solution was treated with H_2S gas for an hour; no precipitate separated.

A mixture of 500 m.grms. Sb and 2 m.grms. Sn as metals was treated with HNO_3 , the mixture evaporated, the residue dissolved in 48 per cent HF, the solution diluted with eight times its volume of water, and treated with H_2S gas for thirty minutes; the precipitate next filtered out, the filtrate evaporated with 3 c.c. H_2SO_4 , and the solution diluted and treated with granulated zinc and a piece of platinum, as long as gas evolution continued; then to the mixture strong HCl was added, and heat applied till the zinc was all dissolved, and the solution was filtered and added to HgCl_2 ; a small white precipitate, which turned black on treatment with NH_4OH , resulted. The experiment was repeated with 500 m.grms. Sb and 1 m.grm. Sn; no precipitate of HgCl_2 was obtained.

Five c.c. 48 per cent HF and 40 c.c. water were saturated cold with H_2S and kept so, while portions of 1 m.grm. Pb as $\text{Pb}(\text{NO}_3)_2$ were added till a permanent precipitate resulted; 6 m.grms. Pb were required.

P. 31, N. 3.—One m.grm. Sb as Sb_2O_3 was dissolved in 5 c.c. 48 per cent HF and 25 c.c. water, and H_2S passed in at the room temperature for thirty minutes; no precipitate formed. The solution was then cooled in ice water, and H_2S again passed; a distinct precipitate separated. The mixture was heated till the precipitate re-dissolved, then cooled to room temperature, again saturated with H_2S (whereby no precipitate was produced), diluted with 15 c.c. water, and again saturated with the gas; a distinct precipitate resulted.

500 m.grms. Sb as metal were treated with HNO_3 , the acid evaporated, the residue dissolved in 5 c.c. 48 per cent HF and 40 c.c. cold water, H_2S passed in half-an-hour, the precipitate filtered out, the filtrate evaporated to fuming with 1 c.c. H_2SO_4 , diluted with water (whereupon a large white precipitate separated), and H_2S passed into saturation; an orange precipitate not very different in quantity from that that separated from the HF solution was obtained.

A solution of 500 m.grms. Sn as SnO_2 and 1 m.grm. Sb in 5 c.c. 48 per cent HF and 40 c.c. water was saturated with H_2S in the cold; a decided orange-coloured precipitate separated.

One m.grm. Sb was dissolved in a mixture of 5 c.c. 48 per cent HF, 40 c.c. water, and 1 c.c. H_2SO_4 (1.84), and H_2S was passed in to saturation in the cold; no precipitate formed. The experiment was repeated with 2 m.grms. Sb; a distinct, compact, orange precipitate separated.

Two m.grms. As as As_2O_3 were dissolved in 5 c.c. 48 per cent HF and 40 c.c. water, and H_2S passed into the cold solution for fifty minutes; no precipitate whatever separated. The solution was then heated on a steam-bath, and H_2S again passed in; a precipitate appeared almost immediately.

A mixture of 400 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$, 2 m.grms. Ta, 2 m.grms. Ti, 2 m.grms. Sn, and 4 m.grms. W, dissolved in 5 c.c. 48 per cent HF and 40 c.c. water, was treated with H_2S , first cold and then hot; the solution became very dark coloured, but very little precipitate separated. Then 3 c.c. H_2SO_4 (1.84) were added; a very bulky, slimy precipitate instantly separated, causing the solution almost to gelatinise. The mixture was filtered;

* From the *Technology Quarterly*, xvii., No. 3.

the liquid ran through with extreme slowness. The filtrate was tested by the complete procedure for all of the elements present in small quantity; no test for any of them except tantalum was obtained, indicating that they were carried down by the slimy precipitate.

P. 33, N. 2.—100 m.grms. dehydrated H_2SiO_3 were dissolved in HF, H_2SO_4 was added, and the solution was evaporated to complete dryness; no residue could be seen, showing that one evaporation with HF and H_2SO_4 suffices to expel all the silica.

P. 33, N. 4.—500 m.grms. Sn as H_2SnO_3 , 300 m.grms. Ti as H_2TiO_3 , 100 m.grms. Nb as Nb_2O_5 , 100 m.grms. Ta as Ta_2O_5 , and 500 m.grms. Mo as MoO_3 were dissolved in separate experiments in a little HF, 2—3 c.c. H_2SO_4 (1·84) were added, the solution was evaporated till it fumed strongly, and then after cooling it was poured gradually into 5 c.c. cold water; no permanent precipitate separated in any case; the molybdenum solution had a deep blue colour, and before dilution there were blue spots above the surface of the liquid. The experiment was repeated with 100 m.grms. Nb, and with 100 m.grms. Ta, taking no especial care to cool the H_2SO_4 upon dilution; a large white flocculent precipitate separated in each case.

To 2 m.grms. W were added 2 c.c. HF, 0·5 c.c. HNO_3 , and 3 c.c. H_2SO_4 ; the solution was heated gently until most of the HF was expelled; it was then heated at 110° in a hot closet for thirty minutes; and finally it was added to 8 c.c. water; a precipitate separated almost immediately.

The experiment was repeated, except that the mixture was heated on a sand-bath just below the fuming-point for thirty minutes; upon dilution a precipitate began to separate.

To 2 m.grms. W and 4 m.grms. W as Na_2WO_4 , 2 c.c. H_2SO_4 (1·84) were added, and the solution evaporated to the fuming-point; even after cooling, the solution remained clear. The liquid was added to 5 c.c. water; a white turbidity appeared in three to five minutes in the 4 m.grms. portion, and in thirty minutes in the 2 m.grms. portion; on standing over-night, yellow precipitates had settled out in both cases. The experiment, with some variations, was many times repeated with 1 m.grm. W; in no case did any precipitate separate, even on standing.

100 m.grms. W as Na_2WO_4 were dissolved in a little water, 1 c.c. H_2SO_4 (1·84) added, and the mixture evaporated to the fuming-point; a large quantity of a heavy yellow powder separated.

P. 34, N. 3.—0·1 m.grm. PO_4 as Na_2HPO_4 was added to 5 c.c. of the $(\text{NH}_4)_2\text{MoO}_4$ reagent, and the mixture was warmed; a considerable yellow precipitate formed at once.

P. 35, N. 2.—To 300 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$, 300 m.grms. W as Na_2WO_4 , and 300 m.grms. V as Na_3VO_4 in separate experiments, 10 c.c. water, 3 c.c. NH_4OH , and 10 c.c. $(\text{NH}_4)_2\text{S}$ were added, and the mixture kept at 50 — 60° for forty-five minutes; everything stayed in solution in the case of the molybdenum and tungsten; a rather small green precipitate remained in the case of the vanadium; the molybdenum had a deep orange-red colour, the vanadium a yellow-brown colour. The experiment was repeated with 1 m.grm. Mo; a distinct orange colour was apparent.

Three portions of 500 m.grms. Sn as metal were treated with three portions of 5 c.c. HNO_3 (1·42), to one of which had been added 500 m.grms. V as Na_3VO_4 , to another 500 m.grms. W as Na_2WO_4 , and to the third 500 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$. The mixture was evaporated to dryness, the residue heated for one hour at 120° , and then treated by P. 5, 6, 33, and 35; on adding an excess of NH_4OH , nothing remained undissolved in the mixture containing vanadium, there was a yellowish white precipitate in that containing tungsten, and a greyish blue one in that containing molybdenum. On adding 10 c.c. cold $(\text{NH}_4)_2\text{S}$, the mixtures containing vanadium and molybdenum became deep red, and no precipitate remained; in that containing tungsten, everything also dissolved.

A solution of 300 m.grms. Ti and 5 m.grms. W in HF was treated by P. 33, 35, 36, and the first paragraph of

P. 38; a decided white precipitate was produced in the HgCl_2 solution, showing the presence of tungsten in the well washed $(\text{NH}_4)_2\text{S}$ precipitate. The experiment was repeated with many other mixtures of titanium and tungsten, with the same result.

As to the impossibility of completely removing tin and tungsten from niobium and tantalum with $(\text{NH}_4)_2\text{S}$, see Hall, "Observations on the Metallic Acids," thesis submitted to University of Pennsylvania, 1904, p. 9.

A mixture of 400 m.grms. Ti and 200 m.grms. Mo was dissolved in HF and treated by P. 33 and 35, the precipitate being three times washed with hot water upon the filter with the help of suction; it still had a strong orange colour. It was returned to a casserole, and heated with frequent stirring upon a water-bath with 10 c.c. NH_4OH (0·90) and 40 c.c. water; the precipitate was then filtered out and washed; it now had only a slight yellowish colour. It was dissolved in HF, and treated by the whole of P. 38; a large precipitate was obtained in the first HgCl_2 test, but none whatever in the second HgCl_2 test after the fusion with Na_2CO_3 and S, showing that the quantity of molybdenum retained in the $(\text{NH}_4)_2\text{S}$ precipitate after digestion with NH_4OH is not so great that it cannot be removed by the fusion. The experiment was repeated, except that the $(\text{NH}_4)_2\text{S}$ precipitate was only well washed with water, not digested with NH_4OH ; in this case a large precipitate was obtained in the HgCl_2 test, even after the fusion with Na_2CO_3 and S, showing that the digestion with NH_4OH may be necessary.

P. 36, N. 2.—100 m.grms. Ti as H_2TiO_3 and 100 m.grms. Nb as Nb_2O_5 , in separate experiments, were dissolved in HF and treated by P. 33, 35, and 36; the whole H_2TiO_3 precipitate dissolved in the H_2O_2 , and of the HfNbO_3 not more than 1 m.grm. remained undissolved. The experiment was several times repeated with 300 m.grms. Ti as H_2TiO_3 ; in every case a large white precipitate, amounting to from one-third to one-sixth of the original quantity, remained undissolved. This precipitate was treated successively with two fresh portions of H_2O_2 and HCl; each time the liquid was strongly coloured, but there was still a large residue. This residue was treated with 5 c.c. cold HF; it dissolved completely in two or three minutes.

Twenty m.grms. Ta as Ta_2O_5 were dissolved in HF, and the solution treated by P. 33, 35, and 36; the H_2O_2 solution was saturated with SO_2 and NH_4OH added; a precipitate about equal in amount to the residue undissolved by the H_2O_2 was produced. This residue was dissolved in HF, and again treated by P. 33, 35, and 36, and the H_2O_2 solution was saturated with SO_2 , and made alkaline with NH_4OH ; again a precipitate nearly equal in amount to the residue was obtained.

One m.grm. Ta as Ta_2O_5 in HF solution was treated by P. 33, 35, 36, and 37, and the H_2O_2 solution obtained in P. 36 was saturated with SO_2 , and made alkaline with NH_4OH ; about one-half the $(\text{NH}_4)_2\text{S}$ precipitate dissolved in the H_2O_2 , and from the residue a distinct precipitate of $\text{K}_2\text{TaF}_7 \cdot \text{Ta}_2\text{O}_5$ was obtained by P. 37.

300 m.grms. Sn and 300 m.grms. Ti in HF solution were treated by P. 33, 35, and 36; there was a large residue insoluble in H_2O_2 and HCl. This was removed from the filter and warmed with 48 per cent HF; a large residue still remained. This was fused with Na_2CO_3 and S, and treated with hot water; the mass dissolved completely, showing the absence of much titanium. The solution was tested for tin by P. 39, 41 (omitting the ignition), and 43; a very large precipitate of HgCl resulted.

P. 36, N. 3.—Two portions of 20 m.grms. Ti in HF solution were evaporated with 2 c.c. H_2SO_4 (1·84), the solution diluted with 5 c.c. water and a large excess of NH_4OH , and heated on a steam-bath for one hour; the precipitates were filtered off, washed, and transferred to test-tubes; to one of them 10 c.c. hot 3 per cent H_2O_2 , and to the other a hot mixture of 10 c.c. 3 per cent H_2O_2 and 2 c.c. HCl (1·12) were added, and the mixtures shaken for two minutes; in the first case, much of the precipitate

was undissolved, and the mixture had a light yellow colour; in the second case, a clear deep orange-red solution resulted.

P. 36, N. 4.—0.1 m.grm. Ti and 100 m.grms. Ti were added to 10 c.c. H_2O_2 and 2 c.c. HCl (1:12); a distinct yellow colour resulted in the first case, and a deep orange-red in the second.

P. 36, N. 5.—Five m.grms. V and 20 m.grms. V as Na_3VO_4 were added to 10 c.c. 3 per cent H_2O_2 and 2 c.c. HCl (1:12); an orange-yellow colour resulted in the first case and a deep orange-red in the second. The experiment was repeated with 5 m.grms. W as Na_2WO_4 ; no colour was produced. It was repeated with 5 m.grms. Mo and with 100 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$; a very pale yellow colour, not so strong as that produced by 0.1 m.grm. Ti, resulted in the first case, and a deep pure yellow colour in the second case.

P. 37, N. 2.—One m.grm. Ta as Ta_2O_5 and 10 m.grms. SiO_2 were dissolved in HF , and, omitting the usual evaporation with HNO_3 , K_2CO_3 was immediately added, the solution was evaporated, the residue heated and dissolved in a little water, and the solution boiled down to 1 c.c.; no precipitate separated, even on standing.

P. 37, N. 3.—For the solubility and composition of the potassium fluotantalate and fluoxytantalate, see Marignac, *Ann. Chim. Phys.*, 1866, (4), ix., pp. 268, 269.

A portion of 2 m.grms. Ta was treated by P. 37, and two other portions of 2 m.grms. Ta were treated in the same way except that the residue, after adding K_2CO_3 and evaporating, was in one case heated only till it became dry (but not enamel white), and was in the other case heated to redness; scarcely any precipitate formed in the portion heated only to dryness, a fairly large precipitate of the usual appearance separated in that treated exactly according to the procedure, and a lighter, more bulky, powdery one resulted in the portion heated to redness.

P. 37, N. 4.—For the solubility of K_2TiF_6 , see Marignac, *Ann. Chim. Phys.*, 1866, (4), viii., p. 65.

P. 37, N. 5.—100 m.grms. Nb as HfNbO_3 , precipitated from H_2SO_4 solution by NH_4OH , were dissolved in HF , and treated by P. 37; at the end a large granular precipitate separated in the cold when the volume was 1.5 c.c., but this dissolved on heating, and after 1 c.c. more of water was added, it remained in solution even after cooling.

The experiment was repeated with a mixture of 100 m.grms. Nb and 1 m.grm. Ta; at the end, when the volume was 1 c.c., the large granular precipitate separated as before, and this dissolved when 3 c.c. water were added, but there then remained a small quantity of the heavy, dirty white precipitate characteristic of tantalum.

For the solubility and composition of the potassium fluoxyniobate, see Marignac, *Ann. Chim. Phys.*, 1866, (4), viii., p. 28.

P. 38, N. 3.—Direct experiments confirmed all the statements in regard to the colours produced.

P. 38, N. 4.—Reduction of TiO_2 by zinc to Ti_2O_3 , see König and v. d. Pfordten *Ber. Chem. Ges.*, 1889, xxii., p. 2079.

Reduction of Nb_2O_5 by zinc to Nb_2O_3 , see Osborne, *Am. Journ. Sci.*, 1885, xxx., (3), p. 333.

One m.grm. Nb as Nb_2O_5 , a mixture of 2 m.grms. Nb and 100 m.grms. Ti, and one of 1 m.grm. Nb and 100 m.grms. Ti were, in separate experiments, dissolved in HF , 1 c.c. H_2SO_4 (1:84) added, and the mixture evaporated till the acid fumed; the solution was then treated with HCl and Zn , and tested with HgCl_2 by P. 25; a distinct silky white precipitate formed immediately in each case.

The experiment was repeated with 100 m.grms. Ti, 10 m.grms. Ta (previously freed from niobium by precipitation as $2\text{K}_2\text{TaF}_7 \cdot \text{Ta}_2\text{O}_5$), and with 100 m.grms. Sn as oxides, and with 300 m.grms. Zr as $\text{Zr}(\text{SO}_4)_2$ in separate experiments; in every case the HgCl_2 solution remained perfectly clear. The experiment was several times repeated with 300 m.grms. Ti as H_2TiO_3 from three different commercial sources; no precipitate formed at once or for a

few minutes in the HgCl_2 solution, but a turbidity always appeared in fifteen minutes, and this increased on longer standing.

The experiment was repeated with 100 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$, with 100 m.grms. V as Na_3VO_4 , and with 4 m.grms. W as Na_2WO_4 in separate experiments; a large precipitate was produced in the HgCl_2 solution in each case.

For evidence of the reduction of WO_3 to WO_2 , see v. d. Pfordten, *Ber. Chem., Ges.*, 1883, xvi., p. 508; of MoO_3 to MoO_2 (when air is not completely excluded), see v. d. Pfordten, *Ber. Chem. Ges.*, 1882, xv., pp. 1925—1929; of V_2O_5 to V_2O_4 , Roscoe, *Ann. Chem. Suppl. Bd.*, 1867, vi., p. 94. The colour changes are also there described.

Mixtures of 300 m.grms. W and 300 m.grms. Ti, of 5 m.grms. W and 300 m.grms. Ti, and of 300 m.grms. Ti and 300 m.grms. Mo, in separate experiments, were dissolved in HF , and treated by P. 33, 35, 36, and 38; in every case a rather large precipitate was produced when the third of the solution was treated with Zn and tested with HgCl_2 . After the fusion of the remainder with Na_2CO_3 and S, the second test with Zn and HgCl_2 resulted in no immediate precipitate in the case of the last two of these mixtures, and in a slight turbidity (less than that given by 1 m.grm. Nb) in the first mixture. The experiment with this first mixture was repeated with the same result.

Two m.grms. Nb and 200 m.grms. Ti in one experiment and 2 m.grms. Nb alone in another were dissolved in HF , evaporated with 2 c.c. H_2SO_4 (1:84), and treated by the last paragraph of P. 38; a considerable precipitate of HgCl was obtained in each case, that with the niobium alone being smaller, probably owing to difficulties of manipulation in the process. But in some of the test analyses (see the next chapter), 2 m.grms. Nb disappeared between the first and second tests with HgCl_2 in the processes connected with the fusion.

P. 38, N. 5.—A mixture of 300 m.grms. Ti as H_2TiO_3 , and 5 m.grms. W as Na_2WO_4 in HF solution, was treated by P. 33 and 35. The $(\text{NH}_4)_2\text{S}$ filtrate was then acidified with H_2SO_4 (1:20), the precipitate tested for tungsten by P. 43, and the filtrate by P. 40; no precipitate (of H_2WO_4) was obtained in either case. The $(\text{NH}_4)_2\text{S}$ precipitate was then fused with Na_2CO_3 and S, and the fused mass treated with water as in P. 38; the aqueous solution was acidified with H_2SO_4 (1:20), and the precipitate tested by P. 43 and the filtrate by P. 40; no precipitate of H_2WO_4 resulted from the treatment of H_2SO_4 precipitate, but a small, though very distinct, compact yellow residue was obtained from the filtrate. The residue from the Na_2CO_3 and S fusion that was insoluble in water was dissolved in HF by a half-hours' digestion, and treated by the first paragraph of P. 38; no precipitate of HgCl was obtained, showing that the tungsten had been completely separated from the titanium by the Na_2CO_3 and S fusion.

For the complete separation of tin and tungsten from niobium and tantalum by fusion with Na_2CO_3 and S, see Hall, "Observations on the Metallic Acids," 1904, p. 9, thesis submitted to the University of Pennsylvania.

(To be continued).

Method of Detecting very Small Quantities of White Phosphorus.—Rudolf Schenck and E. Scharff.—White phosphorus, even when present in very small quantities, ionises the air, while P_4S_3 , which resembles it in luminescence, has no such action. This property can be employed to detect very small quantities of white phosphorus in P_4S_3 . The presence of 0.004 m.grm. can be demonstrated by this test, and it is thus far the most delicate known. By slowly burning the sesquisulphide no P_4O_6 is formed, and this is the cause of the difference in the actions of P_4S_3 and white phosphorus.—*Berichte*, xxxix., No. 6.

A REVISION OF THE ATOMIC WEIGHTS OF SODIUM AND CHLORINE.*

By THEODORE WILLIAM RICHARDS
and
ROGER CLARK WELLS.

(Continued from p. 239).

THE RATIO OF SODIC CHLORIDE TO SILVER.

SINCE the time of Gay-Lussac, the method of titration has been a favourite way of determining ratios between silver and soluble halogen salts. If the end-point were definite, this method would be capable of extreme accuracy. It involves no transference, collection, or weighing of a precipitate; consequently the introduction of silica or alkali from a glass-stoppered flask, occlusion of sodic nitrate, loss of asbestos, and other sources of error, are altogether avoided. After weighing the factors in the proper proportions, dissolving and precipitating, one has only to withdraw a portion of the mother-liquor and determine whether or not the true end-point of the reaction has been reached. It is not strange, therefore, that many eminent experimenters adopted this method in order to determine many atomic weights. The solubility of silver chloride, however, was a fact which Gay-Lussac, Pelouze, Dumas, and many others, as well as Stas in his earlier experiments, did not consider; in consequence, all used the wrong end-point. In his last experiments Stas, recognising the solubility of argentic chloride, attained the end-point in two ways. The first method consisted in titrating to the extreme limit with sodic chloride, and then running back to the opposite extreme limit with silver nitrate; the true end-point was assumed to be half-way between the two limits.† The second method consisted in bringing the mother-liquor to such a point that two portions of it gave equal opalescent precipitates with silver nitrate and sodic chloride respectively; this was the end-point established by Mulder. Before accepting this latter method, Stas attempted to prove for himself that a solution of silver chloride in water gave an equally intense opalescent effect with an excess of argentic nitrate and sodic chloride. He concluded that the opalescence in the two cases was identical, but at the same time admitted that the opalescent precipitates were extremely unstable, and varied continuously in appearance from the moment of precipitation to the time they had settled out completely ("Oeuvres," i., 158). At first, not hoping to improve essentially in this respect upon the methods of Stas, we used this end-point, and after a few preliminary trials made eight careful determinations, using in all 33·1035 grms. of pure salt and 61·0898 grms. of pure silver. The atomic weight of sodium calculated for the average of these experiments was 23·032, with maximum and minimum of 23·040 and 23·023 respectively.

These experiments were of value as giving practice in the manipulation, but the extreme variation was so much greater than it ought to have been that clearly some undiscovered cause of variable error was present in the results.

A study of all the possible causes of irregularity eliminated all probabilities except the uncertainty of the end-point. The purity of the salt and the silver left nothing to be desired, for the same samples gave constant results when the argentic chloride was weighed. Occlusion had been precluded by the use of solutions of not much over decinormal strength, and the mechanical operations were so extremely simple as to leave little opportunity for error. Hence much time was spent in investigating the opalescent phenomena attending the precipitation of traces of argentic chloride. The improved and precise nephelometer served excellently in this tiresome research (see Richards and Wells, *Am. Chem. Journ.*, 1904, xxi., 235). We found that its readings could always be depended upon, and that if any irregularity occurred the fault was with the precipitate within the liquid, and not in the means of observing this precipitate.

The first step in these tests was to prepare a solution of

pure argentic chloride, free from excess either of silver or of chlorine. For this purpose pure floccy silver chloride was very thoroughly washed in a flask by decantation. From time to time two nephelometer tubes were filled with the clear decanted wash-water; to one was added a millilitre of argentic nitrate solution, which contained a milligram of silver, and to the other a millilitre of an equivalent solution of sodic chloride. After stirring, these tubes were examined in the nephelometer within ten or fifteen minutes, and the intensities of the two opalescences were compared. No regularity could be detected in the results, successive trials varying over 50 per cent from one another. For example, in one trial the tube containing an excess of silver was twice as intense in opalescence as the other; while in the following trial, with equal proportions of the same solution, it was only two-thirds as intense as the other. The average of a dozen comparisons confirmed approximately Stas's and Mulder's statement that argentic chloride gives equal opalescence with the two precipitates, but the wide variations between the extremes emphasizes Stas's conclusions as to the uncertainty of the results.

Subsequent experiments showed that the presence of an electrolyte greatly accelerated the formation of the precipitate, indicating a colloidal transition stage. The preceding experiments had been almost free from electrolyte, and in view of this inference, it is easy to see why the formation of the precipitate had been so irregular, for slight differences in the extent and speed of mixing might cause important differences in the coagulation of the colloid. Clearly, in making nephelometric experiments, an excess of electrolyte must be present. Other possible causes of error, such as the effect of light and the presence of absorbed argentic nitrate or common salt in the precipitated argentic chloride from which the solution was made, were carefully guarded against in the further experiments. In order to avoid possible hydrolysis, nitric acid was always added.

(Mulder, "Die Silber-Probirmethode," 1859, p. 72. Some of Mulder's observations in this direction may have been due to occluded material, but the danger of hydrolysis is not wholly to be despised).

Even when all these precautions had been taken, however, incomprehensible irregularities were still present in the results. It was then found that the time allowed for the formation of the opalescence had not been adequate; that in some cases one tube had clouded much faster than the other, but that in all cases neither tube had attained maximum intensity. Often as much time as eight hours was needed for the attainment of this maximum; but the time must not be too greatly extended, or some of the precipitate will be deposited on the bottom of the tube. The performance of the precipitation when chloride is in excess is thus not wholly parallel with that when silver is in excess, already discussed on p. 202.

In view of these facts a new comparison was made. A quantity of silver chloride was precipitated in red light from cold decinormal solutions of silver nitrate and sodic chloride, washed twelve times with water weakly acidified with nitric acid, and eight times further with pure water, the last washings being made in absolute darkness. Pure water containing such quantities of nitric acid and sodic nitrate as would occur in an actual mother-liquor from a quantitative precipitation, was then added, and the mixture was allowed to stand with occasional agitations for a day. In making the nephelometer observations on the decanted liquid, sufficient time was allowed for the precipitates to become constant. Three completely separate trials were made in the nephelometer, and of these are recorded below the depths of liquids which seemed to be equally opalescent.

Observation.	Time.	Tube + AgNO ₃ .	Tube + NaCl.
65	After eight hours	98 m.m.	100 m.m.
66	" "	100	100
67	" "	103	100
Average		100·3	100

* Published by the Carnegie Institution of Washington, April, 1905.
† "Oeuv.," i., 755. This is unsatisfactory for many reasons. See Richards, *Proc. Amer. Acad.*, 1893, xxix., 82.

These observations, made with great care, settled every doubt about the correctness of the equal opalescence end-point. Thus it is clear that Stas encountered difficulties with this method only because he, like all the previous experimenters, did not wait long enough to allow the opalescence really to establish itself in the absence of electrolyte to hasten precipitation.

In the course of these experiments several subordinate points were noted which are worth recording. When the opalescent precipitates were made directly in the tubes from sodic chloride and argentic nitrate, having first one and then the other in excess, the speed of formation was not like that observed when a solution of argentic chloride was treated with the two electrolytes. In the former case, the maximum opalescence was attained more slowly, and the tube containing an excess of chloride always became cloudy much more rapidly than that containing an excess of silver, while in the latter case the difference was much less marked. This adds to the evidence that the dissolved argentic chloride is appreciably colloidal, and that the formation of this colloidal portion requires time.

The possible effect of light upon this end point was another circumstance of interest, although not of immediate bearing on our quantitative work, since actinic light had been scrupulously excluded. In order to ascertain the effect of light, the solution already tested in Observations 65, 66, and 67 was agitated in the flask for an hour at a distance of about 30 c.m. from a white incandescent electric light. Observations 68 and 69 were made with the mother-liquor. It was then agitated in diffused daylight for another hour, an exposure which made the precipitate decidedly bluish, and Observations 70 and 71 taken.

Observation.	Tube + AgNO ₃ .	Tube + NaCl.
68	100 m.m.	100 m.m.
69	100	100
70	97	100
71	100	100
Average ..	99	100

The solution thus gave the same result in the nephelometer as before. Böttger, in his study of the solubility by the conductivity method, also observed that the conductivity did not sensibly alter until the conductivity vessel was exposed to strong light for a considerable length of time. A slight colouring of the precipitate made no difference (*Zeit. Phys. Chem.*, 1904, xlvii., 521). The explanation must be that chlorine thus set free does not ionise. According to Vogel (*Gilbert's Annalen*, lxxii., 286), silver sub-chloride is insoluble in very dilute nitric acid. Hence neither an excess of ionised silver nor chloride should appear in the mother-liquor. Light, therefore, could not have been the cause of any of the variations in preceding observations, and its complete exclusion had been supererogatory.

Having thus, by many experiments, of which those given above are merely samples, assured ourselves that the true end-point may be decided by equality of opalescence when sufficient time is allowed to complete the opalescent precipitation, it became an important matter to make a conclusive series of analyses by this method.

In the first place, a given piece of the purest silver was carefully weighed, and was dissolved in a flask upon the steam-bath. For every gm. of silver about 3 millilitres of nitric acid, of density about 1.20, were used. This density was secured by mixing pure distilled nitric acid of the usual concentration with an equal volume of water. After the silver was dissolved, more water was added, and the nitrous fumes were expelled by a brief very gentle ebullition. A tower of bulbs, ground to fit the neck of the flask, prevented any loss of silver nitrate during the operations. A special experiment proved the efficiency of the bulbs as a means of retaining spray. In this manner of treatment nitric acid always remained in slight excess.

Assuming a probable value for the atomic weight of sodium, the exact weight in air of salt equivalent to the weight of the given piece of silver was calculated and weighed out for fusion. There was always a slight loss of weight when the salt was fused in the platinum crucible, and if, after fusion, more than a m.grm. of salt was still required, approximately the required amount of well-dried salt was added at once by a platinum spatula. The amount so added never exceeded a few m.grms., and its introduction could have caused no error, since in our laboratory salt was not hygroscopic. The exact weight of salt corrected to vacuum was obtained. Any further still slighter lack of equivalence was then made up by volumetric addition of the proper quantity of the same solutions which were to bring the mother-liquor to equal opalescences after the precipitation. Of course the recorded weights include all these small additions.

Both salt and argentic nitrate were diluted to a concentration about fifth normal, and were then mixed in complete darkness with all possible precautions, the argentic nitrate being very slowly poured into the salt solution. When in a day or two the precipitate had settled and the mother-liquor had become clear, the latter was examined nephelometrically.

It was found to be convenient, in determining the amount of a deficiency of either silver or chloride, to calculate once for all the extent of this deficiency in terms of the ratio of lengths of the two nephelometer columns giving equal apparent opalescence. This was in the first place calculated by means of the law of concentration effect; but practically a slightly different value, based upon experience, was found to be more accurate. A ratio of 100 m.m. to 80 m.m. was found to signify an excess or deficiency of 0.15 m.grm. of silver per litre, and other amounts in proportion. Since the average of many readings was probably accurate within 2 per cent and the volume rarely exceeded a litre, it would appear that the end-point was determined within 0.02 m.grm. of silver. This does not, of course, prove that the results are accurate to within this small margin, because other experimental details may have led to larger error. The difference between the maximum and minimum results corresponds, indeed, to a much greater uncertainty, as will be seen. Hence the end-point is determined precisely enough for our purpose.

(To be continued).

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, May 7th, 1906.

Mr. A. GORDON SALAMON in the Chair.

"Notes on the Gutzeit Test for Arsenic." By J. A. GOODE and F. MOLLWO PERKIN, Ph.D.

Owing to the difficulty of obtaining zinc free from arsenic the authors used an ammonium salt—preferably the chloride—and metallic magnesium. Numbers are given showing the solution potential of magnesium in ammonium chloride, and sulphuric and hydrochloric acids, also the difference produced by the addition of cadmium salts. The potential found was always lowered by the addition of the cadmium salt.

Attempts to obtain a permanent stain were unsuccessful. The authors, however, do not consider that this is a matter of great importance, because as the test is so readily carried out it is easy to conduct several experiments simultaneously. One to produce a standard stain, one a blank, and the other with the substance under examination.

The authors found that mercuric bromide is more

delicate than mercuric chloride and the stain is more intense. With mercuric bromide it is possible to detect 1/2000 m.grm. of arsenic.

Although magnesium and ammonium chloride were employed by the authors, they also used zinc and acids, and obtained results equally as good. In fact, they consider that zinc and acid is fractionally more sensitive than magnesium and an ammonium salt.

"*The Separation of Brucine and Strychnine by Nitric Acid—Influence of Nitrous Acid.*" By W. C. REYNOLDS, B.Sc., A.R.C.S., and R. SUTCLIFFE.

The authors have examined the processes proposed by Keller (*Zeit. Oesterr. Apoth. Ver.*, 1893, 542), Stoeder (*Ned. Tydschr. Pharm.*, 1899, xi., 1—5), and Gordon (*Arch. Pharm.*, 1902, ccxi., 641), and show under what conditions brucine can be completely oxidised with the minimum loss of strychnine. They have also investigated the part played by nitrous acid in the oxidation, and the action of alkalis on the products.

"*Absorption of Gallic Acid by Organic Colloids.*" By W. P. DREAPER, F.I.C., and A. WILSON, B.Sc.

The absorption of gallic acid by silk and hide powder is shown to be of a similar nature to its absorption by gelatin or albumin. The influence of general reagents and the curves obtained indicate that the reactions are due to absorption. The precipitation of these colloids by tannic and gallic acids indicates when studied in detail that the solution state is a determining factor in the production of these coagula. The influence of gallic acid on the nature of a tannic acid gelatin coagulum is also observed. The results confirm the pseudo solution theory of dyeing, and indicate the nature of tanning.

FARADAY SOCIETY.

Ordinary Meeting, May 15th, 1906.

DR. F. MOLLWO PERKIN, Treasurer, in the Chair.

MR. H. D. LAW, B.Sc., read a paper entitled, "*Behaviour of Platinised Electrodes.*"

The author desired to find an electrode on which the reduction of the aromatic aldehydes and similar easily reducible compounds could not be effected. Platinised platinum, as being the metal from which hydrogen is liberated at the lowest potential, was tried as the cathode in an acidified alcoholic solution of benzaldehyde. At first, energetic reduction took place; the activity of this, however, diminished in successive experiments, and was extremely small after twelve hours' polarisation. The cause of the reaction is obscure; it is probably catalytic in its origin.

Dr. N. T. M. WILSMORE drew attention to Tafel's work, which the author's results appeared to contradict.

Dr. F. MOLLWO PERKIN remarked on the differences between lead and platinum electrodes, and discussed the general bearing of the author's experiments.

MR. JULIUS L. F. VOGEL, M.I.E.E., M.I.M.M., read a paper on "*The Electrolysis of Fused Zinc Chloride in Cells Heated Externally.*"

The author begins by explaining that the work which formed the subject of the paper was carried out for the most part between 1898 and 1901, and could be conveniently divided into three periods. He then explains how the investigation came to be undertaken; the original inception of the process was due to the late F. Maxwell Lyte, who took out patents for a complex ore process involving the electrolysis of fused zinc chloride and for the dehydration of zinc chloride. The process as such was never investigated practically. The second period deals with the investigation of the dehydration of zinc chloride by evaporating under reduced pressure, and the electrolysis of the salt in a fused state in externally heated cells by Dr. O. J. Steinhart and the author jointly on behalf of the Smelting Corpora-

tion, Ltd. The various experiments and the apparatus employed for these experiments are described. The third period deals with the further investigations made after the United Alkali Company had joined the Smelting Corporation in testing the process, and details are given of the work as carried out under the joint supervision of the author's firm and the chemical staff of the United Alkali Company. The author describes how the process was carried successfully to a stage when continuous electrolysis was carried on for eleven days and nights, and three hundredweight of pure zinc was produced.

He then explains how, on the failure of the Smelting Corporation, the work was suspended, and finally abandoned, although further elaborate investigations were undertaken by the United Alkali Company utilising cells heated internally by the current.

The author finally reviews the work done in cells heated externally, and expresses his opinion that the process was "non-proven," and that it still offers possibilities of being carried to commercial success.

The paper is illustrated with sectional drawings of apparatus, and lantern slides, prepared from photographs of the actual plant, were exhibited.

Dr. O. J. STEINHART referred to the production of zinc from zinc oxide by feeding the latter into a molten bath of chloride, after the fashion of aluminium electrolysis.

Mr. W. MURRAY MORRISON mentioned some of the advantages of internal heating with regard to local inequalities of temperature.

Dr. H. BORNS referred to the formation of zinc clouds diffused in the electrolyte under certain conditions, and consequent reduction of efficiency, observed by Lorenz. He asked whether the addition of impurities, such as ammonium chloride, had been tried. Evaporating with HCl was a method of dehydrating the chloride.

Mr. L. GASTER asked for information regarding comparative energy losses in externally and internally heated cells, and also regarding the consumption of carbon.

Dr. G. RUDORF (communicated), after reviewing the various methods proposed for dehydrating the chloride, affirmed that the author's was the only practicable one. He asked for information regarding the effect on the enamel of continuous heating with zinc chloride; his experience was that a perfect enamel was not obtainable.

Mr. J. L. F. VOGEL, in reply, said that the use of a fused metallic cathode and proper temperature and other conditions prevented the formation of zinc cloud. Carbon losses depended greatly on the dehydration; they had not had opportunities of trying Acheson graphite. It was undesirable to add foreign substances, as these would accumulate in time; it was likewise impracticable to dehydrate in the fashion referred to by Dr. Borns. The difficulty in electrolysis a solution of ZnO in fused chloride was that the solubility was slight, and at the high-current densities demanded by practice not sufficient oxide would pass into solution.

NOTICES OF BOOKS.

The Principles and Practice of Iron and Steel Manufacture. By WALTER MACFARLANE, F.I.C. London, New York, and Bombay: Longmans, Green, and Co. 1906.

The scope of this book coincides very nearly with that of the Iron and Steel Manufacture Syllabus of the City and Guilds of London Institute, and it will be found of great use to the student who is taking such a course of instruction. The practical aspect of the subject receives special attention, the author's experience in iron and steel works having enabled him to go into many of the processes more minutely than is usual in books of this kind, and at the same time to make his accounts both vivid and

interesting. A novel feature characterising the book is the reversal of the usual order of treating the subjects, so that the working and selection of pig-irons is considered in the first part, while the second part deals with the composition of the ores, the construction and equipment of the blast-furnace, and the production of pig-iron; this is a plan which possibly has some advantages to recommend it, and in any case the order of the two sections could readily be inverted, as each section, and indeed each chapter, is quite complete in itself. A special chapter by H. W. Waldron on the treatment of tool-steel gives a short but interesting account of the hardening of steel in practice. The chief defect of the book appears to be the devotion of much space to the most elementary chemical considerations with which every student nowadays would probably be perfectly familiar before he began his technical training, and even supposing he were quite ignorant of chemistry, he would not find enough in the book to explain the reactions occurring during the manufacture of iron, and would consequently be bound to fall back upon the ordinary text-books for further information.

Metallurgical Calculations. By JOSEPH W. RICHARDS, A.C., Ph.D. Part I. New York: McGraw Publishing Company. 1906.

THE series of articles which appeared from March, 1905, to March, 1906, in the *Electrochemical and Metallurgical Industry*, and of which the greater part of this book is a reprint, was well worth preserving in the more convenient form in which it is now published. The importance for metallurgists of acquiring skill in making calculations cannot be over-estimated, not only for the purpose of determining the real efficiency of the various processes, for which it goes without saying that such calculations are absolutely essential, but also for the consolidation of their theoretical knowledge. For the latter purpose, the collection of unworked problems contained in this book will be found well adapted, many of the examples being of considerable difficulty. The book is also worthy of the attention of others besides metallurgical chemists, for it contains many useful hints on the most expeditious methods of solving the mathematical problems met with in general chemistry; thus, examples are included on weights and volumes of gases, and on elementary thermo-chemistry, for which tables of heats of formation are given. The applications of thermo-chemistry occupy a large part of the book, and artificial furnace-gas is also treated very fully, while the principles of the conduction and radiation of heat are not neglected.

Grundriss einer Entwicklungsgeschichte der Chemischen Atomistik. ("Outlines of the History of the Development of the Chemical Atomistic Doctrine"). By Dr. RICHARD EHRENFELD. Heidelberg: Carl Winter. 1906.

THIS introduction to the study of the history of chemistry is marked by great thoroughness, and will appeal more especially to those who are interested in the investigations and theories of the earliest natural philosophers. Beginning with the speculations of Anaxagoras and Empedocles, the author traces the gradual development of the atomistic view of the ultimate constitution of matter as expounded by the three Grecian atomistic philosophers, and gives a review of Plato's Theory of Matter and Aristotle's Doctrine of the Elements. Passing to later times, we find Boyle's Corpuscular Theory fully worked out in connection with the systems of Descartes and Gassendi; the work of this last philosopher, whose claims to recognition are often overlooked, is discussed fully, and a just estimate of its true value given. The treatment of Dalton's hypothesis presents no specially new features, while the chapters on the electron theory are very slight, although the author shows that, had he allowed himself more space for the discussion of this branch of the subject, he might have produced an interesting account of the work of modern investigators in this region.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 6, 1906.

Properties of Liquid Nitrogen.—H. Erdmann.—Liquid nitrogen is a very mobile clear colourless liquid, differing markedly in its physical properties from liquid air; this latter contains much oxygen, and its specific gravity is so high that a piece of ice thrown into it always floats, while in liquid nitrogen both ice and absolute alcohol sink as soon as the temperature has adjusted itself, and the violent evolution of gas, which first of all forces the frozen alcohol and ice to the surface, has ceased. This phenomenon is in better agreement with the specific gravity given by Ramsay and Drumman (0.7914 at the boiling-point) than with that determined by Dewar (0.850). If liquid air is poured over a bulb filled with dry oxygen at ordinary pressures and then closed, no visible change occurs in the interior, but if liquid nitrogen is used the oxygen at once condenses into bluish drops. Thus the temperature produced by the evaporation of liquid nitrogen is lower than that produced by liquid air, and for this reason it is a very good cooling agent. It is a good solvent for liquids boiling at a low temperature. The miscibility of liquid nitrogen with liquid ozone is very striking. A 15 to 20 per cent solution of ozone in liquid oxygen remains perfectly clear after the addition of many times its volume of liquid nitrogen, but if ozonised oxygen is led directly into liquid air, phenomena occur from which it might appear that ozone is salted out from its solution in oxygen by means of liquid nitrogen. Solutions of ozone in liquid nitrogen might be used to determine the molecular weight of ozone in solutions. The author has determined by the surface tension method the molecular weight of liquid nitrogen, but will not publish the results until he has repeated the experiments with chemically pure nitrogen of constant melting-point. Liquid nitrogen appears to be as indifferent as the gaseous element, extinguishing a burning chip and magnesium wire, but if poured over burning metallic calcium, calcium nitride is formed; this yields ammonia with water.

Action of Hydrogen Peroxide on Phosphorus.—Th. Weyl.—Yellow phosphorus when warmed with water yields hydrogen phosphide. Six per cent hydrogen peroxide begins to act on yellow phosphorus at 60°, the resulting products being hydrogen phosphide, which is not spontaneously inflammable, phosphorous acid, and phosphoric acid. The excess of phosphorus which has not taken part in the reaction is converted finally into a horny mass, which yields hardly any fumes in the air, but burns in a flame like ordinary phosphorus. The action of hydrogen peroxide on amorphous and on Schenck's phosphorus is far more energetic. When a peroxide containing more than 8 per cent is used, the action is very violent, and much heat is evolved. The products of the action are hydrogen phosphide, phosphorous acid, and phosphoric acid. When boiling water acts on amorphous phosphorus, hydrogen phosphide is formed, and also (and in much greater quantity) when 5 per cent caustic soda acts on amorphous phosphorus. This development of hydrogen phosphide from amorphous and Schenck's phosphorus by the action of boiling water, caustic soda, and hydrogen peroxide is not to be ascribed to the presence of yellow phosphorus in the preparations, for equal amounts were obtained when all traces of yellow phosphorus were previously removed. Possibly phosphorous acid is first formed according to the equation $3\text{H}_2\text{O}_2 + 2\text{P} = 2\text{P}(\text{OH})_3$, and this is then converted into hydrogen phosphide and phosphoric acid as follows: $-4\text{P}(\text{OH})_3 = \text{PH}_3 + 3\text{PO}(\text{OH})_3$, while a part of the phosphorous acid is oxidised to phosphoric acid by the excess of hydrogen peroxide.

Constitution of Chromic Acid.—W. Manchot.—On investigating quantitatively the oxidation of uranous oxide by means of chromic acid in presence of hydriodic acid it is found that one atom of uranium replaces three equivalents of oxygen, using up two equivalents itself, while the other is transferred to the hydriodic acid. The three equivalents are released simultaneously, which leads to the conclusion that in chromic acid the three equivalents of oxygen are directly connected with one another. Hence the formulæ appear to be $O=Cr<\overset{O}{\underset{O}{\parallel}}$ and $\overset{HO}{\parallel}Cr<\overset{O}{\underset{O}{\parallel}}$ rather than $Cr\overset{O}{\parallel}\overset{O}{\parallel}\overset{O}{\parallel}$.

Oxidation of Ammonia to Compounds of Nitrogen and Oxygen.—Otto Schmidt and Rudolf Böcker.—The authors have investigated the oxidation of ammonia to nitric acid, nitrous acid, and hyponitrous acid by the use of catalytic agents, paying special attention to the yield. Using platinum and platinum asbestos they obtained 75 to 76 per cent of the ammonia used as oxygen compounds, and in some cases more than 80 per cent. The first product is nitric oxide. This is then rapidly converted by the excess of oxygen into nitrous acid anhydride, which amounts to about 80 to 90 per cent of the total products, the residue being nitric acid. Bayer has found that ammonia is oxidised by the air or by oxygen in presence of pyrites under certain conditions, and it seems probable that this might be a profitable process to employ commercially, as the yields are good. On the other hand, Ostwald's process of oxidising ammonia by free oxygen to nitric acid by contact substances, *e.g.* platinum, would not be a lucrative process at present prices.

Atomic Weight of Nitrogen.—Philippe A. Guye.—Determined by physico-chemical methods the mean of many experiments gave for the atomic weight 14.008, and by chemical methods it was found to be 14.010. The International Atomic Weight Committee has retained the number 14.04, which the author believes to be erroneous for the following reasons:—1. It was determined by the old methods, which rested on very indirect relations between the atomic weight of nitrogen and that of silver. These methods were not exact enough to guarantee the accuracy of the second figure in the decimal. 2. The new value $N=14.01$ results from twelve determinations of the direct ratio to oxygen, and this element is the actual basis of all other atomic weights. Six of these determinations were performed by physico-chemical and six by chemical methods. 3. Chemists have always been in the habit of taking $N=14$ for rough calculations, and this differs from the true value by only 1/1400, and, moreover, agrees perfectly with the accurately determined densities of the gases nitrogen, nitrous oxide, nitric oxide, and ammonia, and with exact analyses of the gases nitrous oxide and nitric oxide.

Constituent of Phosphorised Air which causes Electric Conductivity.—Rudolf Schenck, F. Mihr, and H. Banthien.—The examination from the chemical point of view of the substance which causes the ionisation of the air in the neighbourhood of white phosphorus has shown that it cannot be due to ozone. Nor does the oxidation of organic substances, such as oil of turpentine, cotton, wood, &c., by ozone produce any conductivity, although it is accompanied by luminescence phenomena. The authors have examined a whole series of oxidation processes which closely resemble those of phosphorus; *e.g.*, that of bromoacetylene, CH_2CBr , and have found no trace of the formation of ions. Thus, apparently the oxidation process in the case of white phosphorus is not itself the cause of the ionisation, which is to be sought rather in the secondary processes which are possibly conditioned by the occurrence of oxidation processes. It has been found that the conductivity continues only as long as oxidation is going on. All factors which prevent oxidation also prevent the appearance of the conductivity phenomenon; *e.g.*, oil of turpentine, carbon disulphide vapour. It is

known that the oxidation of white phosphorus ceases in pure oxygen at atmospheric pressure. The authors have now shown that pure oxygen which has passed over phosphorus causes a very much smaller leakage of electricity than air under the same conditions. The addition of small quantities of ozone to the pure oxygen causes a powerful increase in the conductivity, and the same conductivity is obtained if pure air, after it has been in contact with white phosphorus, is led over or through the following substances:—Oil of turpentine, alcohol, mesitylene, ammonia, ethylene, amylene, &c. The cause of the conductivity thus lies, not in the oxidation process as such, but in the presence of an oxidation product of phosphorus. The substances which prevent oxidation prevent the formation of the product, but cannot in themselves influence the ionisation. Red phosphorus also yields the so-called phosphorus emanation. The authors have investigated the action of the vapours of phosphorus trioxide on the electroscope, and have found that the action is very strongly marked, so that there can be no doubt that this substance is responsible for the conductivity.

MISCELLANEOUS.

Estimation of Cadmium in Volatile or Organic Salts.—H. Baubigny.—When a cadmium salt precipitated from its solution by hydrogen sulphide gas is a volatile one, such as the chloride or bromide, a distinct error in estimation may be caused, owing to traces being left in the sulphide. In order to eliminate this error it is necessary to obtain the sulphate from the sulphide by a very careful method. The sulphide is detached from the filter after washing and without previous desiccation. The precipitate rapidly sinks in water, and the clear liquid above can be decanted. After thorough washing by this method the merest trace remains on the filter-paper, and therefore a negligible trace of volatile salt. After incineration of the paper, the residue can be added to the sulphide and the whole be transformed into sulphate. By this method the evaporation of the washing water is avoided which would necessitate the re-dissolving of the sulphide on the filter. The results obtained are most accurate. In the case of an organic salt of cadmium a decided excess of sulphuric acid is added to the solution. If this acid is insoluble, it is filtered and washed with acidulated water; if it is soluble, as the decomposition of the salt is almost integral in presence of sulphuric acid, the method may be proceeded with as in the former case without any fear of loss.—*Comptes Rendus*, cxlii., No. 17.

MEETINGS FOR THE WEEK.

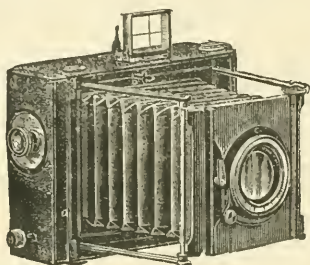
- TUESDAY, 5th.—Royal Institution, 5. "Northern Winter Sports—Sweden and its People," by Col. V. Balck.
WEDNESDAY, 6th.—Society of Public Analysts, 8.
THURSDAY, 7th.—Royal Institution, 5. "Man and the Glacial Period," by Prof. W. J. Sollas, F.R.S.
— Chemical, 8.30. "Ammonium Selenate and the Question of Isodimorphism in the Alkali Series," by A. E. H. Tutton. "An Improved Beckman Apparatus for Molecular Weight Determination," by J. M. Sanders. "Resolution of Lactic Acid by Morphine," by J. C. Irvine. "Vapour Pressures of Binary Mixtures—Part I., Possible Types of Vapour Pressure Curves," by A. Marshall. "Action of Sodium on *aa*-Dichloropropylene," by I. Smedley. "Thiocarbamide as a Solvent for Gold," by J. Moir. "Action of Sulphur Dioxide and Aluminium Chloride on Aromatic Compounds," by S. Smiles and R. Le Rossignol.
FRIDAY, 8th.—Royal Institution, 9. "Studies on Charcoal and Liquid Air," by Prof. Sir James Dewar, D.Sc., F.R.S., &c.
— Physical, 8. "Solution of Problems in Diffraction by the Aid of Contour Integration," by H. Davies. "Effect of Radium in Facilitating the Visible Electric Discharge *in vacuo*," by A. A. Campbell Swinton. Mr. J. Gool'd's Experiments with a Vibrating Steel Plate, exhibited by Messrs. Newton and Co. "Fluid (Liquid) Resistance," by Col. de Villamil.
SATURDAY, 9th.—Royal Institution, 3. "Inspiration in Poetry," by Prof. W. Macneile Dixon, M.A., &c.

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ON

RADIO-ACTIVE SUBSTANCES.

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THE CHEMICAL NEWS

AND

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THE CHEMICAL NEWS.

VOL. XCIII., No. 2428.

A NEW PRODUCT OF ACTINIUM.

By O. HAHN.

RECENTLY the attention of investigators has been drawn to the remarkable similarity in the nature of the radio-active decay of thorium and actinium.

Thorium, itself inactive, yields as its first product radio-thorium (O. Hahn, "Jahrb. Radioact. Elektr.," II., 330), which emits α -rays. Then follow thorium X, the characteristic emanation, and finally the "active deposit." (for this expression see Hahn, "Ueber Einige Eigenschaften der α -Strahlen des Radiothorium," *Physikal. Zeit.*). Actinium behaves in exactly the same way. By means of the same methods as led to the separation of thorium X from thorium, Godlewski (*Phil. Mag.*, July, 1905), and, independently, Giesel (*Berichte*, 1905, xxxviii., 775) separated from actinium a new product, actinium X. This yields the emanation, which in its turn gives the active deposit.

Moreover, the similarity between actinium and thorium is still greater. I have succeeded in finding in actinium a new product which lies between actinium and actinium X, and which may be called "radio-actinium" from analogy with thorium. The substance emits α -rays, decays to the half value in about twenty days, and then yields actinium X, which in its turn decays to the half value in 10^2 days.

The separation of radio-actinium from an actinium solution in radio-active equilibrium is effected as follows:—A very fine precipitate is produced in the solution, and this gradually settles and carries down the new product with it, while the greater part of the actinium and actinium X remains in solution. Amorphous sulphur was found very suitable for this purpose. A small quantity of sodium thiosulphate was added to a fairly strong acid solution of actinium and hydrochloric acid, and the slight precipitate was allowed to settle in the cold. After filtering and washing, the precipitate was examined for activity. It showed a strong α -radiation, but, comparatively speaking, hardly any β -radiation nor any emanation. The activity of the α -rays increase, until after about three weeks a maximum is reached. The activity is then about two to three times as strong as directly after preparation.

The activity then begins to decrease slowly, finally with a half-value period of about twenty days, following an exponential law.

The activity of the β -rays and the power of emanation, both insignificant shortly after the preparation of the radio-actinium, increase very strongly, reach their maximum at the same time as the α -rays, and then decrease at the same rate as the latter.

The first rise of the activity to a maximum depends on the formation of actinium from radio-actinium. Thus if we separate off the actinium X when the activity of the radio-actinium begins to exhibit a decrease, the residue first becomes stronger again, and behaves in exactly the same way as the freshly prepared radio-actinium. The actinium X separated decays with its characteristic period of ten days.

Some experiments of Dr. Levin, performed in this Institute and soon to be published, are important in considering this question. He prepared actinium X in the usual way with ammonia. But he did not succeed in reducing the α -activity of the filter to the small fraction which had been obtained by others. An investigation of his still strongly active precipitate showed that its powers of emanation was practically zero, and thus actinium X was out of the question. As actinium itself has been

found to be almost inactive, the observed α -activity indicated another product, which is radio-actinium.

Actinium itself, free from radio-actinium and actinium X, emits practically no α - nor β -rays, then slowly increases in activity and reaches a maximum after about four months.

Godlewski (*Phil. Mag.*, July, 1905) obtained an almost inactive actinium, a proof that, without knowing it, he had separated the radio-actinium from it.

I have observed that on dissolving actinium in hydrochloric acid, mostly only a small quantity remains undissolved, and this small amount contains a large proportion of radio-actinium.

Giesel has recently announced that his emanium preparations increase in activity for about six months. This may possibly be explained by assuming that radio-actinium is formed.

In a communication which has recently appeared, Marckwald (*Berichte*, 1905, xxxviii., 2264) compared the chemical properties of actinium and emanium with one another, and came to the conclusion that actinium and emanium are not identical, but are genetically related, viz., actinium is a decay product of emanium, as the activity of actinium disappears in the course of a few months, but actinium and not emanium is the cause of the interesting emanation. This is contradictory to Debiere's statement that his actinium does not decrease in activity.

The decaying substance described by Marckwald, which he takes for Debiere's actinium, is possibly the new product radio-actinium, for a thorium precipitate with sodium thiosulphate brings down radio-actinium too. It is then not explained why his product did not increase in the beginning, or why he did not succeed in getting actinium X from it.

It must be mentioned that the above experiments were performed both with Debiere's actinium and also with Giesel's emanium. The result was always the same.

A full description of the experiments will be given elsewhere.—*Berichte*, 1906, xxxix., 1605.

ON THE USE OF GYPSUM FOR THE RECOVERY OF AMMONIA AS A BY-PRODUCT IN COKE MAKING.

By H. WARTH.

As there must be many localities in which sulphuric acid is not available in sufficient quantity for the production of ammonium sulphate, the following experiments were made to demonstrate the possibility of using gypsum instead of sulphuric acid. Gas-water (of 1.02 specific gravity) from the municipal gas works of Birmingham was used for the purpose, and it is assumed that gas-water obtained from a coke-making plant would not differ much from it in composition. The above gas-water was found to contain in 100 c.c. :—

	Grms.
Ammonium chloride	0.7
Ammonium carbonate	5.2
Ammonium sulphide, Am_2S	0.4
Other compounds containing NH_3	0.3

The total of ammonia in 100 c.c. = 2.6 grms. NH_3 , equivalent to 10.0 grms. ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$.

To begin with, a sample of the gas-water was evaporated to dryness, with the loss of most of the ammonia. The residue contained only enough ammonia to make it equivalent to 1.1 grms. ammonium sulphate per 100 c.c. of gas-water.

A sample of the same original gas-water was then evaporated to dryness after having been mixed with an excess of hydrochloric acid. By this all the ammonia was

recovered. The residue was dissolved in water and boiled with sodium hydrate. The ammonia which was evolved was caused to be absorbed by a measured volume of standard hydrochloric acid. The amount of ammonia was then ascertained by titration with standard sodium hydrate solution and methyl-orange. 100 c.c. gas-water yielded 2.6 grms. NH_3 , equivalent to 10.0 grms. ammonium sulphate.

A quantity of the original gas-water was now well shaken with plaster-of-Paris; this changed all the ammonium carbonate present into sulphate, whilst a corresponding amount of the calcium sulphate was changed into carbonate. Of the clear fluid (Solution 2, sp. gr. 1.04) thus obtained, 100 c.c. were now evaporated to dryness; this operation liberated and removed a portion of the ammonia, leaving only the newly-formed ammonium sulphate and the small quantity of original ammonium chloride. By titration the quantity of ammonia present in the residue was found equivalent to 8.0 grms. of ammonium sulphate. We had thus recovered 80 per cent of the ammonia, chiefly as ammonium sulphate, without the use of sulphuric acid.

Another sample of the above-mentioned solution No. 2 was now boiled for sufficient time to expel all free ammonia, and it was arranged that this free ammonia was absorbed by standard hydrochloric acid. The ammonia absorbed per 100 c.c. solution No. 2 amounted to an equivalent of 1.7 grms. ammonium sulphate, or 17 per cent of the entire ammonia in the original gas-water. As the previous solution yielded 80 per cent, the two operations combined would yield 97 per cent of the entire quantity of ammonia. It would be possible to carry this out on a large scale. We could recover 97 per cent of the ammonia by means of gypsum, and by means of only about one-sixth of the sulphuric acid which would have been required without the use of gypsum. Solution No. 2 would first be boiled and made to yield its liberated ammonia to sulphuric acid, and afterwards it would be concentrated so as to produce crystallised ammonium sulphate.

By the use of ferrous sulphate it would also be possible, if desired, to do without sulphuric acid altogether. The gas-water would again be first treated with gypsum (or plaster-of-Paris) and the sediment of calcium carbonate carefully removed, so that the clear solution could now be treated with ferrous sulphate. The bulky precipitate of ferrous sulphide was, in our experiment, filtered off, and, after evaporating the solution, the residue yielded 95.4 per cent of the entire ammonia.

Treatment of the gas-water with gypsum, ochre, and carbon dioxide only yielded 85.7 per cent of the entire ammonia. The above-mentioned methods are thus much superior, and especially the first one with a limited use of sulphuric acid, appears most advantageous.

Birmingham, May 24, 1906.

A REVISION OF THE ATOMIC WEIGHTS OF SODIUM AND CHLORINE.*

By THEODORE WILLIAM RICHARDS
and
ROGER CLARK WELLS.

(Continued from p. 239).

THE RATIO OF SODIC CHLORIDE TO SILVER (*continued*). The final series of experiments, given below, includes only those experiments in which every known source of error was avoided. In order to illustrate the details of the method, the full record of a single experiment, in so far as it does not repeat what has already been described, is here given.

Experiment 53.

Weight of sodic chloride, in vacuum (Sample I) . . . 5.08685 grms.
Weight of silver, in vacuum (Sample O) . . . 9.38819

These were dissolved and mixed on February 2, 1904. After two hours' agitation the mixture stood until next day, when an examination was made with the nephelometer. Two test-tubes were filled with the mother-liquor by means of a clean pipette, withdrawing 0.07 litre for this purpose. The two solutions were very nearly equal in opalescence. With occasional shaking the mixture was therefore allowed to stand yet another day, in order to ensure the thorough solution of possibly adsorbed material. The subsequent proceedings are summarised below:—

February 4 (0.07 litre withdrawn).

Time of standing in nephelometer.	Nephelometer readings.		
	(a) Reading of tube with excess AgNO_3 .	(b) Reading of tube with excess NaCl .	$a \div b$.
Thirty minutes	45	54	0.83
Two hours ..	43	54	0.80
Eighteen hours	46	55	0.83

This reading indicates a slight deficiency of silver. Hence 0.15 m.grm. of silver in solution was added to the residual mother-liquor, and the mixture was occasionally shaken.

February 8 (0.070 litre withdrawn).

Time.	Nephelometer readings.		
	a.	b.	$a \div b$.
Five minutes	48	30	1.60
Sixteen hours	60	57	1.05

There was now a slight *excess* of silver. Hence there was added 0.03 m.grm. of sodic chloride, corresponding to 0.06 m.grm. of silver.

February 16 (0.07 litre withdrawn).

Time.	Nephelometer readings.		
	a.	b.	$a \div b$.
Fifteen minutes	50	39	1.28
One hour	50	44	1.14
Two hours	50	46	1.09
Twelve hours	53	54	0.98
	36	35	1.03
	55	59	0.93
	33	33	1.00
	70	67	1.04
	52	53	0.98
	37	38	0.97
	24	23	1.04
	360	362	1.00

Thus precise equality had been attained.

Volume liquor now remaining 435 c.c.
Withdrawn during trials 280 "

Original volume 715

If the first addition of Ag had been made to the original total mother-liquor it would have been $0.15 \times \frac{715}{575} = 0.19$

m.grm. Similarly, $0.06 \times \frac{715}{505} = 0.08$ m.grm. Hence extra silver required to produce equal opalescence in original mother-liquor = $0.19 - 0.08$ m.grm. = 0.00011 gm.

Total silver = $9.38819 + 0.00011 = 9.38830$ gm. This silver contained 0.0037 per cent of impurity. Weight of pure silver present 9.38795. Then $\text{Ag} : \text{NaCl} = 9.38795 : 5.08685 = 100.000 : 54.185$.

Molecular weight $\text{NaCl} = 107.930 \times 54.185$, if

$\text{Ag} = 107.930$ 58.482

If atomic weight Cl 35.455

Atomic weight of sodium 23.027

* Published by the Carnegie Institution of Washington, April, 1905.

Ten such complete analyses are recorded in the table below.

*The Ratio of Sodid Chloride to Silver.
Final Series.*

Exp.	Preparations.		Weight salt (in vac.).	Observed weight silver (in vac.).	Correct weight of purest silver (vac.).	Parts NaCl equivalent to 100,000 parts silver.
	NaCl.	Silver.	Grms.	Grms.	Grms.	
41.	F	N	3.96051	7.30923	7.30896	54.187
44.	K	N	2.32651	4.29371	4.29355	54.186
46.	K	N	5.36802	9.90736	9.90699	54.184
45.	G	M	4.00548	7.39237	7.39210	54.186
47.	G	N	4.69304	8.66133	8.66101	54.186
52.	H	P	3.27189	6.03864	6.03842	54.185
53.	I	P	5.08685	9.38830	9.38795	54.185
55.	J	P	3.66793	6.76977	6.76952	54.183
56.	L	P	5.48890	10.13030	10.12993	54.185
57.	L	P	3.55943	6.56933	6.56909	54.185
			41.42856	—	76.45752	54.185

The agreement of these results is now as good as could reasonably be expected. Whereas the earlier similar experiments, made before time enough had been allowed for the full development of the opalescence, showed an extreme variation in the results of 0.017, this extreme variation is now only 0.004. Since in these last experiments seven different specimens of salt were used, and three different specimens of silver, it seemed hardly probable that further work in the same direction would add certainty to the average. The chemical identity of the various preparations seems to have been proved.

The atomic weight of sodium, calculated from the ratio 100:000 : 54.185, the average of these ten determinations, is 23.027, if silver and chlorine are respectively assumed to be 107.930 and 35.455. This is 0.010 higher than the value obtained by reference to argentic chloride—a difference which seems small in comparison with much quantitative chemical work, but which, nevertheless, is far greater than the sum of the probable experimental errors of the two series of results.

The conflicting outcome of all these carefully conducted experiments thus still remained not easily explicable. Their value for the atomic weight of sodium differed by over 0.1 per cent from Stas's result, and furthermore, as has just been said, the comparison of sodic chloride with silver yielded a higher result, 23.027, than that found by comparison with argentic chloride, 23.017. Both these discrepancies required explanation before the results could be accepted without reserve.

In the first place, much time was spent in the search for some possible error in our results. For example, several of our samples of salt, especially the preparation numbered K, were tested for lithium with the greatest care by fractional treatment with alcohol. The extreme mother-liquors showed no trace of the lighter metal, although in parallel experiments it was found that less than 0.01 per cent of lithium chloride could be detected in this way, even by the simple flame test. This proportion could not affect the atomic weight of sodium by more than 0.002; but since no trace of lithium was found in any of the specimens of our salt tested, it is clear that our low value of the atomic weight could not be due to lithium. The constant results found with differently prepared samples from different sources seemed to exclude the possibility of the presence of the very few other metals which would yield too low a value for the atomic weight, namely, beryllium, magnesium, aluminium, and calcium. Acid could not have been present, since the material was usually prepared from salt finally crystallised from pure neutral solution, and was always fused in air. It gave, moreover, a wholly neutral reaction to methyl orange.

Because no flaw could be found in the operations leading to the new results, the conclusion was inevitable that the old ones were in error. In order to prove this

without question, experiments were instituted in which each one in succession of the gravest faults already pointed out in Stas's work were imitated, in order to detect the individual errors introduced by each.

In the first place, two experiments were made in which the salt was prepared approximately according to Stas's method, the substance being fused with ammoniac chloroplatinate. The salt thus prepared was compared with pure silver by means of the nephelometer, using, as Stas did, the opalescence which had been given only fifteen minutes to form. In this way 2.67137 and 5.51270 grms. of salt needed, respectively, 4.92908 and 10.1717 grms. of silver, corresponding to an atomic weight of sodium of 23.039 in each case. Since the value obtained from salt certainly free from platinum in the same way (p. 253) was 23.032, the difference of 0.007 may probably be ascribed to platinum, which had not been precipitated by thermal decomposition. Presumably, therefore, traces of platinum were present also in Stas's preparations.

In the next place, the effect of the occlusion of sodic chloride by argentic chloride was quantitatively studied. It will be remembered that Stas always dropped dry sodic chloride crystals into his silver nitrate solution instead of adding the salt in the dissolved state. Such a procedure offered the maximum opportunity for the occlusion of sodic chloride. In the following experiments, made with the purest material (salt F and silver P) and executed with all the precautions outlined above, this error alone was purposely committed. After dropping in the solid salt, the mixture, having been shaken two hours, was allowed to stand for a day, all according to the manner of Stas. In three experiments (Nos. 42, 51, 48,) 5.37853, 3.34018, and 5.29539 grms. of salt required, respectively, 9.92510, 6.16392, and 9.77122 grms. of silver, thus giving three determinations of the atomic weight of sodium, as follows: 23.033, 23.033, and 23.036, or on the average, 23.034.

In the last experiment the gradual dissolving of this occluded salt was shown in an indubitable manner. On continued shaking throughout a week, more and more silver had to be added, until finally the mixture came to complete constancy at a point corresponding to 9.77264 grms. of total silver. This quantity gives 23.028 as the atomic weight of the sodium, showing that within a week nearly if not quite all the occluded sodic chloride had been disengaged.

If, then, we sum up the effects which we have found for the three chief errors probably made by Stas in his later work, the following result is obtained:—

Our value of the atomic weight of sodium from the ratio of sodic chloride to silver	23.027
Effect of too prompt reading of opalescence	+23.005
Presence of platinum in salt	+23.007
Occlusion of salt in silver chloride	+23.007

Result which we should have obtained by
Stas's complete method 23.046

This result is so near that found by Stas's assistants in 1881 (23.050) as to make it seem probable that these errors really existed in Stas's work, and that the present investigation avoided them. The acknowledged presence of traces of gas in Stas's silver and silica in his salt may be neglected in this comparison as being errors of mutually opposing tendency and almost equal effect. The rectifying of previous work by means of a later correction is always a doubtful process, and the above table is given only to show that Stas's small mistakes have all been traced.

It is not so easy to give the numerical magnitude of the correction to be applied to Stas's earlier work, which, as has been said, is inconsistent with the later work, because it gives the same result, although a wholly false end-point was used. It is probable, however, that in the early work, carried out by Stas himself, the precipitated argentic chloride was much more thoroughly shaken with its mother-liquor than the later work executed by MM. Nyst and

Cabilliau under Stas's direction. Continued shaking would diminish the solubility of the argentic chloride, as well as disengage the occluded salt. Thus the decrease of the latter error might have balanced the effect of a greater error in the end-point, although this in its turn would be less marked than it would have been had the mixture been less thoroughly shaken.

All these considerations tend to support the present determination as against the verdict of the older ones, but no explanation is yet afforded as to the reason for the difference between the values 23.017 and 23.027 found by different processes in the present work. Long consideration of the matter led finally to the conclusion that the accepted value of the atomic weight of chlorine, 35.455, upon which the calculation depends, must be in error. Accordingly this problem also was attacked experimentally. But before these lengthy experiments are recounted, brief mention must be made of the successful attack upon another doubtful point, which concerns the sodic chlorine.

(To be continued).

A SYSTEM OF QUALITATIVE ANALYSIS INCLUDING NEARLY ALL THE METALLIC ELEMENTS.*

PART II.—ANALYSIS OF THE TUNGSTEN GROUP.

By ARTHUR A. NOYES.

(Concluded from p. 252).

Confirmatory Experiments and References (continued).

P. 39, N. 1.—To two portions of 7 c.c. H_2SO_4 (1.20), NH_4OH was added till alkaline, and then 7 c.c. $(\text{NH}_4)_2\text{S}$, and the mixtures were heated at $50-60^\circ$ for thirty minutes. To one of the mixtures 2 m.grms. W as Na_2WO_4 were added, and both were acidified with H_2SO_4 (1.20), and filtered; a small pink precipitate was obtained from both solutions; but the filtrate from the blank was colourless, while that from the solution containing tungsten was of a pronounced yellow colour. The experiment was twice repeated, using 1 m.grm. in place of 2 m.grms. W; a bright yellow precipitate formed on adding the H_2SO_4 , and the filtrate was distinctly yellow.

A mixture of 6 grms. of Na_2CO_3 and S with 1 m.grm. W in one case, and 6 grms. of Na_2CO_3 and S alone in another, were fused for fifteen minutes, and the fused masses dissolved in water, and the solutions filtered, acidified with H_2SO_4 (1.20), shaken, and again filtered; the mixture containing tungsten gave a yellowish pink precipitate and a slightly yellow filtrate; the blank gave a pale yellow precipitate and a colourless filtrate.

Five m.grms. W as Na_2WO_4 were treated by P. 33, 35, and 39; the precipitate was of a bright yellow colour, much deeper than that of precipitated S; the filtrate was deep yellow. The precipitate was ignited, the residue fused with Na_2CO_3 , the mass dissolved in water, and the solution boiled with HNO_3 ; a small but unmistakable, yellow precipitate of H_2WO_4 was obtained. The filtrate was treated by P. 40; a large yellow precipitate, about ten times as great as that from the H_2SO_4 precipitate, remained.

In regard to the incomplete precipitation of WS_3 by acids from solutions in alkaline sulphides, see also Jannasch and Bettges, *Ber. Chem. Ges.*, 1904, xxxvii., p. 2223.

A mixture of 300 m.grms. Sn and 2 m.grms. W was treated by P. 33 and 35, and the $(\text{NH}_4)_2\text{S}$ filtrate by P. 39; the filtrate was colourless. This filtrate was treated by P. 40; a small but unmistakable yellow precipitate of H_2WO_4 resulted.

The experiment was repeated with a mixture of 300 m.grms. Sn and 10 m.grms. W; a yellow precipitate estimated at 1 m.grm. W was obtained from the filtrate.

A mixture of 30 m.grms. Sn as SnCl_4 , 8 m.grms. W as Na_2WO_4 , and 20 m.grms. PO_4 as Na_2HPO_4 was treated by P. 35, 39, 40, 41, 43, and 44, and the HCl solution of the ignited sulphides obtained in P. 41 was divided, part being evaporated with HNO_3 , and tested with $(\text{NH}_4)_2\text{MoO}_4$, and the remainder evaporated to a small volume, diluted, treated hot with H_2S , filtered, and the filtrate concentrated and tested for tungsten with Zn; no indication of tungsten was obtained either at this last point or in P. 43 or 44; but a strong blue colour resulted at the end of P. 40. Phosphate was present in considerable quantity in the HCl solution, though the sulphide precipitate had been thoroughly washed; also, of course, in large quantity in the H_2SO_4 filtrate.

To a mixture of 200 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$ and 2 m.grms. W as Na_2WO_4 , and to one of 400 m.grms. Mo and 4 m.grms. W in H_2SO_4 solution, were added NH_4OH and 10 c.c. $(\text{NH}_4)_2\text{S}$, and the deep orange-red solution digested at 50° for thirty minutes, and then treated by P. 39; there resulted a black precipitate and a filtrate which was colourless with the first mixture, pale blue from the second. The filtrate was treated by P. 40; no precipitate of H_2WO_4 remained in either case. That from the second mixture was also tested with Zn and KSCN; a pronounced but not very strong red colour resulted.

In certain test analyses, however, where molybdenum and tungsten were both present, the latter was found only in the filtrate, and there in large quantity (see T. A., 34, 36).

One m.grm. Mo and 1 m.grm. Sn in H_2SO_4 solution were separately digested with 10 c.c. $(\text{NH}_4)_2\text{S}$, and the solution acidified with H_2SO_4 ; a dark brown or yellowish brown precipitate separated, and the filtrate was colourless. The filtrate from the MoS_3 was evaporated to a volume of 3 c.c., and Zn and KSCN added; no coloration was produced.

100 m.grms. V as Na_3VO_4 were digested with $(\text{NH}_4)_2\text{S}$ as in P. 33 and 35, the small bluish grey precipitate remaining was filtered out, and the filtrate treated with H_2SO_4 by P. 39; a large brown precipitate and pale blue filtrate resulted, showing that the vanadium was divided.

P. 40, N. 3.—One m.grm. W and 50 m.grms. PO_4 as Na_2HPO_4 were added to 5 c.c. HCl (1.06) and Zn added; a pronounced blue colour resulted.

P. 41, N. 1.—The experiment first described under C. E., G. D., § 10, was repeated with 300 m.grms. W as WS_3 , with 100 m.grms. V as V_2S_5 , and with 100 m.grms. Mo as MoS_3 in separate experiments, except that the sulphides were ignited in a H_2S atmosphere, as directed in P. 41, before heating with the HCl (1.20), the crucible being heated without a jacket over a powerful burner; there was no darkening whatever of the $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution in any of the three cases.

300 m.grms. Sn obtained as SnS_2 by acidifying a $(\text{NH}_4)_2\text{S}$ solution were treated by P. 41, the crucible being heated within a burnt-clay jacket for ten minutes with the full flame of a powerful burner; almost the whole mass (which was black and glistening) dissolved in the hot HCl (1.20), there being only a very small yellow residue. This residue was washed and treated with HNO_3 and HCl, the solution evaporated twice with HNO_3 , and the residue treated with HNO_3 (1.20); only a small turbidity remained.

This experiment was repeated except that the crucible was heated without a jacket and only to a low red heat; the ignited mass was mostly yellowish, but contained some black particles, and it left a large residue of yellow scales with metallic lustre when boiled with HCl (1.20).

This experiment was repeated except that the crucible was heated without a jacket to the highest temperature obtainable with a powerful burner; it was thirty minutes before the whole mass became black; after boiling with HCl (1.20) for twenty minutes, there was still a considerable quantity of a yellow scaly residue.

A mixture of 300 m.grms. Sn and 3 m.grms. W, and one of 300 m.grms. Sn and 1 m.grm. W, obtained as sulphides by adding H_2SO_4 to a $(\text{NH}_4)_2\text{S}$ solution, were

* From the *Technology Quarterly*, xvii., No. 3.

treated by P. 41 and 43; a considerable yellow residue of H_2WO_4 was obtained in the first case, and a small but unmistakable one in the second case.

200 m.grms. Sb as precipitated Sb_2S_3 were treated by P. 41 and 42; the ignited mass consisted of a black button, and this dissolved completely in the HCl (1:20) upon boiling for five minutes.

P. 42, N. 1.—One m.grm. Sn as precipitated SnS_2 was treated by P. 41 and 42, the ignition being continued for twenty-five minutes; a considerable precipitate of HgCl_2 was produced.

Separate mixtures of 300 m.grms. W as Na_2WO_4 with 1 m.grm. Sn, 2 m.grms. Sn, 4 m.grms. Sn (in two experiments), and 10 m.grms. Sn as SnCl_4 were treated with NH_4OH and $(\text{NH}_4)_2\text{S}$, and then by P. 39 and 41, and the HCl solution was then immediately added to HgCl_2 solution; no precipitate was produced in the first three cases (with 1–4 m.grms. Sn), but a fairly large one resulted in the last case (with 10 m.grms.). The experiment was repeated with a mixture of 300 m.grms. W and 1 m.grm. Sn, but the HCl solution was treated by P. 42; a distinct residue of Sn and a decided precipitate of HgCl_2 resulted.

The HCl solutions obtained in the experiments described under P. 41, N. 1, by heating on a steam-bath 300 m.grms. W as ignited WS_2 , 100 m.grms. V as ignited VS_2 , and 100 m.grms. Mo as ignited MoS_2 , with HCl (1:20), were added to HgCl_2 solution; not even a cloudiness resulted in any of the cases. The HCl solution obtained by boiling the ignited Sb_2S_3 with HCl (1:20) was added to HgCl_2 solution; a large precipitate (of SbO_3H_3) separated, but this dissolved completely upon adding HCl.

P. 43, N. 1.—300 m.grms. Mo obtained as MoS_3 by precipitation from $(\text{NH}_4)_2\text{S}$ solution by H_2SO_4 were boiled with 10 c.c. HNO_3 (1:10); apparently all the molybdenum went into solution. The residue was washed and treated repeatedly with a portion of NH_4OH ; the solution was acidified with HCl, and treated with Zn and KSCN; no red coloration appeared.

A mixture of 2 m.grms. W and 500 m.grms. Mo in HF solution was treated by P. 3, 5, 6, 33, 35, 39, and 43; an unmistakable precipitate of H_2WO_4 was obtained.

100 m.grms. Mo and 100 m.grms. V as ignited sulphides were separately warmed on a steam-bath with 8 c.c. HNO_3 (1:42) and 2 c.c. HCl (1:20); in two minutes the residue dissolved completely. The molybdenum solution was evaporated to 3 c.c.; a large precipitate separated.

The experiment was repeated with 300 m.grms. W as ignited WS_2 ; the black residue was completely converted into a yellow one within five minutes.

In regard to the difficulty of separating H_2WO_4 completely by the addition of strong acid to a tungstate solution, see Jannasch and Bettges, *Ber. Chem. Ges.*, 1904, xxxvii., p. 2225.

P. 43, N. 2.—Mixtures of 2 m.grms. W as Na_2WO_4 and 100 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$ (in two experiments), and of 4 m.grms. W and 100 m.grms. Mo were treated by P. 35, 39, 40, 41, and 43; no precipitate of H_2WO_4 was obtained in any case from the H_2SO_4 filtrate tested by P. 40; and no precipitate separated from the HNO_3 and HCl solution of the ignited sulphides even on standing over-night; but upon evaporating this solution with H_2SO_4 , a large yellow residue separated from the mixture containing 4 m.grms. W, an extremely small but distinct one from one of those containing 2 m.grms. W, and nothing whatever from the other containing 2 m.grms. even on standing over-night.

P. 44, N. 1.—0.5 m.grm. W as Na_2WO_4 was added to 2 c.c. HCl (1:12) and a few granules of zinc introduced; a strong blue coloration appeared almost immediately, and in a few minutes blue flocks separated from the liquid. The colour persisted for at least fifteen minutes. The experiment was repeated with 2 m.grms. W; an intensely blue flocculent precipitate separated, and on filtration the mixture yielded a perfectly colourless filtrate.

To 10 m.grms. Mo and 100 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$,

dissolved in a few drops of water, 2 c.c. HCl (1:12) and a few granules of zinc were added; in each case the solution became yellow at once, then dark orange-yellow, next dark green, and finally dark olive-brown, but no precipitate formed except after long standing; at no time was a blue coloration noticeable.

100 m.grms. Mo as $(\text{NH}_4)_2\text{MoO}_4$ were dissolved in 10 c.c. water and 0.5 c.c. HCl (1:12) added; the solution soon assumed a clear blue colour, which became deep blue after some minutes.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 17th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MESSRS. E. Barrett, E. R. Chrystall, J. L. Foucar, P. H. Marsden, H. Martin, J. T. Nance, W. D. Seaton, W. H. Simmons, D. Sommerville, P. F. Spencer, F. W. Storey, R. W. Tonkin, and J. A. Watson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Shelton Gottlieb Agar, Panorama House, Guernsey; Thomas William D. Gregory, 82, Moorland Road, Burslem; John Gerard Hughes, 2, Canute Road, Southampton; Ernest Arthur Jenkinson, Dautsey Agricultural School, West Lavington; William Rest Mummery, The Firs, Shenfield, Essex; Arthur Charles Palmer, B.Sc., 17, Wansbeck Gardens, West Hartlepool; Samuel Shrowder Pickles, B.Sc., The Imperial Institute, S.W.; Willie Macro Seaber, B.Sc., Firdale, Sheen Lane, East Sheen; James Neil Watts, P.O. Eikenhof, Johannesburg, S. Africa.

Certificates have been authorised by the Council for presentation for ballot under By-law I. (3) in favour of Surendra Prasad Sanyal, M.A., Majhowli Raj, Gorakhpur, U.P., India; Allan Sime, Kingston, Jamaica; Edward Jocelyn Wortley, Rectory, Half-way Tree, Jamaica.

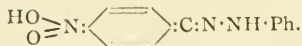
Of the following papers, those marked * were read.

*98. "The Relation between Absorption Spectra and Chemical Constitution. Part VI. The Phenylhydrazones of Simple Aldehydes and Ketones." By EDWARD CHARLES CYRIL BALY and WILLIAM BRADSHAW TUCK.

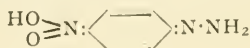
A spectroscopic investigation of the phenylhydrazones of formaldehyde, acetaldehyde, propylaldehyde, acetone, and diethylketone shows that all these compounds exist in two forms, the true hydrazone and the azo-form, in which the hydrogen atom has wandered from the nitrogen atom to the carbon atom of the aldehyde or ketone residue, thus: $\text{Ph}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}_3$ and $\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}_3$. The azo-form is the more stable, and all the above compounds readily pass over into this form under the influence of light, except formaldehyde phenylhydrazone, which polymerises. All the azo-compounds are strongly coloured, owing to the isorropesis between the unsaturated nitrogen atoms and the benzene nucleus. If the compounds are prepared from *p*-bromophenylhydrazine, the change to the azo-form takes place quite slowly; when aldehydes and ketones are allowed to react with *p*-bromophenylhydrazine, the true hydrazone is always produced first, which is not always the case when phenylhydrazine is used, for in certain instances the azo-compound is obtained at once. As is to be expected, true hydrazones which are perfectly stable are produced by the interaction of aldehydes and ketones with phenylmethylhydrazine.

An investigation into the absorption spectra of the hydrazones of the three isomeric nitrobenzaldehydes shows that the colour of these substances is not due to their existence in the azo-form. It is found, however, that they exist in the quinonoid form and are somewhat similar to

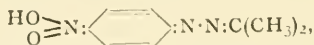
the nitrophenols. The formula of the *para* compound is, in all probability,—



Similarly, in the case of *p*-nitrophenylhydrazine and its acetone derivative, these compounds are quinonoid, thus:—



and—



and are comparable with *p*-nitroaniline.

DISCUSSION.

Mr. W. ROBERTSON asked Mr. Baly if he had examined the spectra of the two pure acetaldehydephenylhydrazones individually, inasmuch as the product of melting-point 80° , found by Mr. Baly to give rise to the absorption band in the ultra-violet, is far from being a pure substance. It would be of considerable interest to ascertain if this band is also shown by either isomeride in the pure state in neutral solvents.

Dr. LANDER asked the authors whether the change of hydrazone to azo-compound was complete, or whether the two substances formed a mixture in equilibrium in solution.

Dr. HEWITT asked Mr. Baly if he had examined any hydrazones obtained from quinolyldiazines. *Ortho*- and *ana*-quinolyldiazines were examined some years back by Dufton (*Trans.*, 1891, lix., 756; 1892, lxi., 782), when it was found that certain of the derived hydrazones, more especially those prepared with *ana*-quinolyldiazine, exhibited brilliant colours. The author did not, however, suggest for them any other than a hydrazone structure (compare Armstrong, *Trans.*, 1892, lxi., 789).

Mr. Baly said that the two isomerides mentioned by Mr. Robertson would, if present, give identical absorption bands. He hoped to extend the work in very many directions, but had not yet examined the substances mentioned by Dr. Hewitt.

*99. "The Rusting of Iron." By JOHN TRENGROVE NANCE.

It is known that ammonium chloride solution accelerates the rusting of iron. The author finds that interaction takes place with evolution of hydrogen and liberation of ammonia; iron passes into solution in the ferrous state, and is not precipitated in the absence of air, owing to the excess of ammonium chloride present.

The solubility of iron in solutions of different concentration does not diminish proportionally with the amount of ammonium chloride present; hence it is probably due to the action of hydrogen ions formed by hydrolysis of the salt, as similar proportional numbers are found for the solubility of iron and for the catalytic effect of the solutions on the hydrolysis of methyl acetate. The rate of rusting of iron in these solutions varies with the concentration in a similar manner, leading to the conclusion that rusting is due to the (mainly catalytic) action of hydrogen ions. In support of this, it is found that the chlorides of weak bases accelerate rusting far more than do those of the strong bases, and that the influence of acids is roughly proportional to their avidities.

DISCUSSION.

Dr. MOODY thought it unfortunate that chemists were not definitely agreed as to the exact meaning to be attached to the term rusting. It appeared desirable that the term should be limited to those changes which metals undergo on exposure to air under normal atmospheric conditions. With regard to the results obtained by the author of the paper under discussion, it must be borne in mind that on heating a solution of ammonium chloride at 80° ammonia would be evolved, and free hydrochloric acid would be formed in solution. In fact, the experiments resolved

themselves into a determination of the attack on iron by solutions of hydrochloric acid of different strengths, and the theoretical conclusions drawn by the author appeared unwarranted.

Dr. F. M. PERKIN agreed with Dr. Moody that the term rusting should be used to denote the atmospheric oxidation of iron, and should not be employed in reference to oxidation by other agencies.

He pointed out that many other metals were dissolved by ammonium salts, and asked whether Mr. Nance had tried the action of ammonium persulphate, which dissolved iron much more rapidly than other ammonium salts. The solution of the metals was evidently due to hydrolysis, and, as ferric salts are much more readily hydrolysed than ferrous salts, the explanation of the rapid solution in ammonium persulphate was to be traced to the conversion of the ferrous salt into the ferric condition. Oxidation of iron might be brought about by any feebly ionised acid. With highly ionised acids, as long as excess of acid is present, no precipitation of hydroxide will take place, but with excess of iron, hydrolysis will ultimately ensue.

In reply, Mr. NANCE said that he considered his results sufficient to prove that atmospheric corrosion and rusting of iron takes place through the catalytic intervention of hydrogen ions.

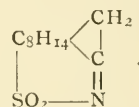
*100. "Aromatic Compounds obtained from the Hydro-aromatic Series. Part II. The Action of Phosphorus Pentachloride on Trimethyldihydroresorcin." By ARTHUR WILLIAM CROSSLEY and JAMES STUART HILLS.

When phosphorus pentachloride acts on trimethyldihydroresorcin, two substances are produced, a liquid boiling at $118-119^\circ$ at 33 m.m., which is 3:5-dichloro-1:1:2-trimethyl- Δ^2 :4-dihydrobenzene, and a solid melting at 76.5° , namely, 3:5-dichloro-1:1:2:6-trimethylbenzene. This aromatic dichloride is converted on oxidation into 3:5-dichlorohemimellitic acid, crystallising from water in transparent, hexagonal plates, containing $2\text{H}_2\text{O}$, and melting at $226-227^\circ$, at which temperature it is rapidly converted into its anhydride. The trimethyl ester crystallises in rhombohedra melting at $62-63^\circ$, and the monomethyl ester melts at $141-142^\circ$.

*101. "Studies of Dynamic Isomerism. Part V. Isomeric Sulphonic Derivatives of Camphor." By THOMAS MARTIN LOWRY and EGBERT H. MAGSON.

Measurements were given of the solubility of a series of twenty sulphonic derivatives of camphor, both alone and in presence of a trace of alkali. The majority of the compounds derived from α -bromocamphor and α -chlorocamphor showed an increase of solubility similar to that observed in these compounds themselves, and in their β - and π -halogen derivatives (Lowry, *Proc.*, 1906, xxii., 70).

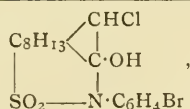
In the case of camphor sulphonamide, a decrease of solubility resulted from the addition of alkali, and it was found that the amide, which crystallises unchanged from acetic anhydride, had been converted quantitatively by N/500 sodium ethoxide in alcoholic solution at 20° into the anhydramide,—



The π -amide derived from α -bromocamphor could not be converted into an anhydramide, but was found to yield an acetyl derivative, the solubility of which was unchanged by the addition of alkali; the compound is therefore

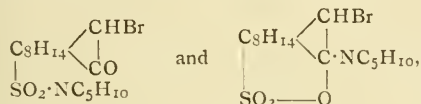
formulated as $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{C}_8\text{H}_{13} \begin{array}{l} \diagup \text{CBr} \\ | \text{C} \\ \diagdown \end{array} \parallel \text{C} \cdot \text{OAc}$.

The β -sulphonanilides derived from α -bromocamphor and α -chlorocamphor dissolve readily in caustic soda and are re-precipitated by acids. Possibly on account of their acid properties, the anilides, which may be formulated as, for example,—



do not increase in solubility when a trace of alkali is added.

The isomerism previously observed in the camphor sulphopiperidides (Armstrong and Lowry, *Trans.*, 1902, lxxxii., 1449) has now been detected in the α -bromopiperidides; both compounds, formulated as—



increase in solubility when alkali is added, and probably exist in stereoisomeric forms.

*102. "The Densities of Liquid Nitrogen and Liquid Oxygen and of their Mixtures." By JOHN KENNETH HAROLD INGLIS and JOSEPH EDWARD COATES.

The authors have determined the densities of liquid nitrogen and of liquid oxygen, and of a number of mixtures of the two liquids at the temperatures 74.70° and 79.07° Abs. on the hydrogen scale. These are the temperatures at which the vapour pressure of pure oxygen is 100 m.m. and 200 m.m. respectively, and they are therefore easily reproduced. The results showed that a slight contraction took place on mixing the two liquids, this contraction being greater at the higher temperature. The densities of the pure liquids differed by about 1 per cent from the values obtained by Baly and Donnan (*Trans.*, 1902, lxxxi., 907). These values of the densities of the mixtures may be used to determine the relation between the partial pressures of nitrogen and oxygen above a mixture of the two liquids and their concentrations in that mixture. It is found that the solubility of nitrogen in oxygen obeys Henry's law; but that the solubility of oxygen in nitrogen does not obey the simple form of that law, for oxygen dissolved in nitrogen is associated to the extent of about 9 per cent.

103. "Glutaconic and Aconitic Acids." By HAROLD ROGERSON and JOCELYN FIELD THORPE.

Ruhemann is mistaken when he states (*Proc.*, 1906, xxii., 137) that we were not fully acquainted with his several publications dealing with these acids.

When we recorded the reactions of γ - and $\beta\gamma$ -alanyl substituted derivatives of 2:6-dioxypyridine (*Trans.*, 1905, lxxxvii., 1682), we compared them with the corresponding reactions of the α -alanyl β -substituted derivatives prepared by Ruhemann (*Trans.*, 1893, lxiii., 876). The γ - and $\beta\gamma$ -derivatives prepared by him (*Trans.*, 1899, lxxv., 245), and which he complains have not been mentioned by us, are α -aryl derivatives containing phenyl and benzyl groups in these positions, and therefore were not, in our opinion, suitable for the purpose of comparison. As a matter of fact, the behaviour of our α -aryl compounds differs in many important respects from that of the α -aryl compounds prepared by him.

Ruhemann has also evidently misunderstood our meaning, since he writes (*loc. cit.*):—"They state that ethyl dihydroxycinchomerate had first been prepared by Errera and Perciabosco, but they overlook the fact that Ruhemann and Stapleton had obtained it the year before." The passage referred to (*Trans.*, 1906, lxxxix., 640) is:—"It is evidently identical with the compound prepared by Errera and Perciabosco by the action of hydrochloric acid on ethyl 2:6-dihydroxypyridine-3:4:5-tricarboxylate." We did not desire to assign priority to Errera and Perciabosco, but merely wished to establish the identity of our compound, an object which seemed to us better attained by referring to the method of preparation adopted by these chemists, rather than to the more indirect process used by Ruhemann and Stapleton.

We have carefully re-read the paper by Ruhemann and Orton (*Ber.*, 1894, xxvii., 3449), and are still of the opinion that the remark (*Trans.*, 1906, lxxxix., 634), "Ruhemann and Orton suggest that aconitic acid corresponds to fumaric acid in constitution, whereas the malenoid form is represented by aceconitic acid," is not an overstatement of the case, since probability surely implies suggestion.

Regarding the criticism of our formulæ for these acids and the remark, that if they were correct, then the action of ammonia on ethyl aconitate might be expected to yield a five-membered ring compound besides citrazinamide, we cannot too strongly emphasise the remarks we made in our reply to Feist and Beyer (*Trans.*, 1906, lxxxix., 650), which were to the effect that our formulæ for these compounds are merely an effort to represent diagrammatically a state of equilibrium between two tautomeric forms.

104. "The Chemistry of Organic Acid Thiocyanates and their Derivatives." By AUGUSTUS EDWARD DIXON.

Compounds of the class R·CO(CNS), when reacting with primary nitrogenous bases, present marked differences of behaviour, according to the nature of the hydrocarbon radicle R. If R be aromatic, these compounds behave in ordinary circumstances principally as thiocarbimides, uniting additively with the base employed to form in each case a symmetrically disubstituted thiocarbamide, R·CO·NCS + R'·NH₂ = RCO·NH·CS·NHR'. On the other hand, if R be a fatty radicle, the function of the associated group, —CO(CNS), varies greatly with the conditions—notably temperature and the nature of the base presented. In such cases, the end-products contain both disubstituted thiocarbamide and a mixture of substituted amide with thiocyanic acid, the latter substances originating through double decomposition: R·CO·SCN + R'·NH₂ = R·CO·NHR' + H·SCN.

The interposition of an oxygen atom between the radicle R and the group CO(CNS), where the former belongs to the aliphatic series, increases the thiocarbimide power of the resultant molecule; thus, phenacetyl "thiocyanate," Ph·CH₂·CO(CNS), and phenoxyacetyl "thiocyanate," Ph·O·CH₂·CO(CNS), readily yield the reaction for thiocyanic acid, whilst carbo-benzyloxy "thiocyanate," Ph·CH₂·O·CO(CNS), does so to a very trifling extent.

A number of substituted thioureas and thiocarbamides are described, resulting from the action of ammonia or other bases on various thiocarbimides, RO·CO·NCS, where R = phenyl, *o*-tolyl, *p*-tolyl, and benzyl respectively.

When acetylphenylbenzylthiourea was heated under diminished pressure, a liquid distilled over having the general properties of acetyl "thiocyanate"; this fact is regarded as confirmatory of Hawthorne's view (*Trans.*, 1906, lxxxix., 566) that acetylthiocyanate is identical with acetylthiocarbamide.

Phenylchlorocarbonate united directly with thiourea to form a compound of formula NH:C(NH₂):S·CO·O·Ph·HCl; on treating with dilute alkali, diphenyl carbonate and thiourea were obtained, and not the corresponding base. Unlike the fatty derivatives obtained from methyl or ethyl chlorocarbonate, the hydrochloride, when decomposed by heating, did not yield a *pseudo*-thiourea, NH:C(NH₂):S·Ph.

105. "The Molybdilactate and the Tungstilactate of Ammonium." By GEORGE GERALD HENDERSON.

The observations recorded in a previous paper (*Trans.*, 1903, lxxxiii., 259) on the influence of molybdc and tungstic anhydrides on the specific rotations of solutions of alkali *l*-lactates pointed to the conclusion that compounds of the type RO₂(C₃H₄O₃M)₂ are formed both when the respective anhydrides are dissolved in hot solutions of the alkali lactates and when alkali molybdates and tungstates are heated with solutions of lactic acid. Attempts have since been made to isolate the molybdi- and tungstilactates so produced, only one of which, namely, potassium molybdilactate, had already been obtained in crystalline form, and then in very small quantity and in a slightly impure state (*Trans.*, 1899, lxxv., 554). The results were disappointing so far as the metallic salts were concerned,

but, on the other hand, well-defined stable ammonium salts of molybdilactic and tungstilactic acids were easily obtained. Thus, finally, crystalline derivatives of the tartar emetic type have been prepared from all the hydroxy-acids which were selected for examination, and in the latter case, as in the others, the author's suggestions regarding the constitution of these compounds are supported by the results of experiment.

Molybdic and tungstic anhydrides are dissolved, the latter with some difficulty, when heated on the water-bath with solutions of alkali lactates. The reaction comes to an end when the substances are present in the proportion of one mol. anhydride to two mols. lactate, and no reduction of the anhydride occurs unless a trace in excess of that amount is added, provided that the solution is not heated to boiling. Addition of alcohol to the concentrated solutions causes the separation of colourless viscous liquids which do not become crystalline even on prolonged contact with the mother-liquor. When left in a vacuum desiccator over sulphuric acid, the syrupy liquids slowly dry to amorphous glassy masses, which are extremely deliquescent, very readily soluble in water, and fairly so in dilute alcohol. Owing to the failure of all attempts to induce these substances to crystallise, they could not be obtained in a satisfactorily purified state, but an analysis of the compound of molybdic anhydride and sodium lactate, partially purified by dissolving in a little water, and precipitating with alcohol, showed that its percentage of sodium was only a little higher, and of molybdenum a little lower, than that required by the formula $\text{MoO}_2(\text{C}_3\text{H}_4\text{O}_3\text{Na})_2$. Similar results were obtained by experiments with calcium and barium lactates. The anhydrides are dissolved fairly readily by hot solutions of these salts, but the compounds formed could not be isolated except as vitreous solids, which analysis proved to be somewhat impure.

The results were different when ammonium lactate was used. Molybdic anhydride was readily dissolved when heated on the water-bath with a solution of the salt, and, as in the case of the metallic lactates, no reduction took place unless a greater proportion of the anhydride than one mol. to two mols. lactate was added. After heating for some time, the solution was concentrated to a small bulk, and, after cooling, a quantity of a crystalline salt separated. The salt was purified by crystallisation from water, dried in a desiccator over sulphuric acid, and analysed:—

1.0 gave 0.097 NH_3 . $\text{NH}_3 = 9.7$.

0.5 „ 0.235 MoS_2 . $\text{Mo} = 28.2$.

$\text{MoO}_2(\text{C}_3\text{H}_4\text{O}_3\text{NH}_4)_2$ requires $\text{NH}_3 = 10.0$; $\text{Mo} = 28.2$ per cent.

Ammonium molybdilactate, $\text{MoO}_2(\text{C}_3\text{H}_4\text{O}_3\text{NH}_4)_2$, forms small colourless crystals which are fairly readily soluble in water and insoluble in alcohol. It is stable in the dry state at the ordinary temperature, but undergoes decomposition with loss of ammonia when heated in a steam-oven. It is also stable in aqueous solution, but is hydrolysed on warming with dilute alkalis or mineral acids. When silver nitrate is added to a solution of the salt, a yellow precipitate is formed which quickly turns black if exposed to light.

Ammonium tungstilactate, $\text{WO}_2(\text{C}_3\text{H}_4\text{O}_3\text{NH}_4)_2$, was prepared and purified in a similar manner. It is a colourless, crystalline salt, closely resembling and apparently isomorphous with the corresponding molybdilactate, than which it is somewhat more stable, as it does not begin to decompose when heated until a temperature of about 120° is reached, when ammonia is evolved. It dissolves in water fairly readily and without change. Analysis of the purified salt, dried at 100° , gave the following results:—

0.5 gave 0.406 NH_3 . $\text{NH}_3 = 8.12$.

0.5 „ 0.268 WO_3 . $\text{W} = 42.5$.

$\text{WO}_2(\text{C}_3\text{H}_4\text{O}_3\text{NH}_4)_2$ requires $\text{NH}_3 = 7.94$; $\text{W} = 42.9$ per cent.

My thanks are due to Mr. Hugh B. Brown for assistance in this work.

PHYSICAL SOCIETY.

Ordinary Meeting, May 25th, 1906.

Dr. C. CHREE, F.R.S., Vice-President, in the Chair.

A PAPER on "Colour Phenomena in Photometry" was read by Mr. J. S. Dow.

The question has often been raised whether it is physiologically possible to compare lights of different colours. The author has found that it is chiefly a matter of practice. A great difficulty arises from the fact that the central portion of the retina is more sensitive to red, and less sensitive to green, than the surrounding portion. Therefore, when we attempt to photometer lights of different colour, enormous differences are found as the distance of the eye from the photometer-screen is altered, and utterly different results are obtained with different photometers. Curves are given in the paper showing the effect of altering the distance of the eye when an incandescent mantle is compared against a gas standard with the Joly photometer. Differences of 5 per cent. can easily be obtained. An experiment was shown at the meeting to demonstrate that the Purkinje Phenomenon, generally regarded as a great cause of uncertainty in ordinary work, only becomes noticeable at very small illuminations and with comparatively large fields of view. The Purkinje effect can be physiologically explained by the action of the "rods" and "cones" on the retina. The comparative weakness of the Purkinje effect with small fields can be explained by the fact that the central portion of the eye contains practically no rods but only cones.

The paper also describes experiments to show that Flicker photometers seem to be affected by colour-phenomena, but to a smaller extent than ordinary ones.

In any case, whether Flicker or an ordinary photometer is adopted, it is necessary to specify the size of the field, the distance of the eye, and the order of illumination used, in order to get consistent results.

Mr. A. P. TROTTER expressed his interest in the paper, and said he thought the difficulty of comparing the intensities of two lights of different colours was an imaginary one. It was possible for anyone accustomed to photometric measurements to get reliable comparisons of lights of different colours. The author, for the sake of precision, had dealt with the comparison of red and green, but he pointed out that in practice the variation in colour between the lights under test was not so great as this; ranging from the light of the Hefner lamp to that of the arc-light or daylight. He agreed with the author that when taking photometrical measurements it was best to get as far away as possible from the comparison disc.

Mr. A. RUSSELL considered Mr. Dow's explanation of the phenomena of heterochromic photometry by means of the irregular distribution of rods and cones on the retina quite satisfactory. Whatever theory we adopt as to the difference between the functions of the rods and cones, it is obvious that their relative numbers on the portion of the retina covered by the image of the photometer-disc is a factor of primary importance in determining the balance. It is a physiological fact that there are no rods on the yellow spot, and this had led Professor Blondel to suggest that if we arranged so that the image always fell on the yellow spot, consistent results might be obtained. Reference was also made to M. Lauriol's paper in the *Bulletin* of the Société Internationale des Electriciens on the effect of the speed of the rotating part of the Flicker photometer on the balance obtained. The experiments proved that many of the results obtained depended merely on the speed of rotation. When comparing green with red, the numbers obtained varied between the wide limits of 1 to 5. Even when comparing a Nernst with an

ordinary glow-lamp, a variation of 20 per cent with speed was noticed. It was pointed out that it was easier to obtain a balance when comparing red with green by using a grease-spot photometer than by using a Lummer-Brodhun contrast photometer. The colours of the two sides of the grease-spot in the position of balance, owing to the transmitted light, were not pure red and green, but were mixtures which it was much easier to compare. The experience of the speaker was that the Lummer-Brodhun photometer was the one most favoured by those engaged in accurate photometric work. For comparing lights of different colours, however, a modified form of grease-spot photometer would have many advantages.

Mr. S. SKINNER described an Automatic Arc-lamp, exhibited by Mr. H. Tomlinson and Rev. G. T. Johnston.

This is a simple form of automatic arc-lamp which can be constructed by any amateur at small expense. A vertical brass tube supported by a wooden framework carries the upper carbon, which can be raised or lowered by hand and clamped in any position in the tube. The lower carbon fits into a hollow brass tube, and into the lower part of the tube is fitted an iron plunger. The plunger is surrounded by a solenoid, consisting of a single layer of No. 14 copper wire, the internal diameter of the solenoid being slightly greater than the diameter of the plunger. The plunger dips into a small box of mercury, and is made to float upright by means of a brass collar and by the rounded ends of three nails forming an equilateral triangle. The current enters the upper carbon through the brass cylinder, passes through the lower carbon into the mercury, and then through the solenoid. To "strike the arc" the lower carbon is raised by hand to touch the upper one, and the plunger is then permitted to sink into the mercury until the suction of the solenoid balances the buoyancy of the mercury. With currents from 2 to 6 amperes the light is very steady, but for currents above 4 amperes it is suggested that the solenoid should have two layers of wire arranged in parallel. For currents less than 3 amperes these layers could be arranged in series.

A paper on "*The Theory of Moving Coil and other kinds of Ballistic Galvanometers*" was read by Prof. H. A. WILSON.

In this paper the exact formulæ giving the quantity of electricity passed through various types of ballistic galvanometers in common use are obtained. It is shown that the different types require different formulæ, all of which, however, reduce to the same formula when the angle of deflection is very small. In the case of a moving-coil galvanometer having a rectangular coil, iron core, and pole-pieces arranged so as to give a radial magnetic field, the formulæ take a simple and convenient form.

Mr. A. CAMPBELL exhibited a Bifilar Galvanometer free from Zero Creep.

For measuring direct currents and voltages of ordinary range (from 0.1 ampere or volt and upwards) moving-coil galvanometers with shunts or added resistances are convenient. The usual instruments, however, are affected by gradual displacement of zero (due to elastic set) when a deflection is maintained for some time. This difficulty is got over by replacing the ordinary torsional suspension by a bifilar system in which the two wires are so far apart that the gravity control quite swamps that due to the torsion of the wires. In the instrument shown, the wires are more than 1 c.m. apart, and the sensitivity with 40 ohms resistance is 400 m.m. at 1 metre for 0.001 ampere; this is sufficient for many purposes. The full deflection may be maintained for hours without causing a zero creep of 1 part in 2000. To attain good damping a very powerful magnet is used. The arrangement of this and the general design are due to Mr. R. W. Paul, who has adapted to the purpose Mr. Evershed's system of coil and magnet.

Prof. H. A. WILSON asked if the zero creep might not be due to magnetic material in the coil. If the field was

unsymmetrical the presence of magnetic material would produce a creep.

Mr. CAMPBELL replied that in very sensitive moving-coil galvanometers the presence of magnetic dirt was a source of trouble, but in the instrument which he had exhibited the control was so strong that the creep due to this cause was practically nothing.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, May 21st, 1906.

Mr. A. GORDON SALAMON in the Chair.

"*The Electro-Chemical Problem of the Fixation of Nitrogen*. By Prof. PHILIPPE A. GUYE.

The author demonstrates the importance of the problem of the fixation of nitrogen by recalling the principal statistics relative to the total consumption of Chilean nitrate and of ammoniacal salts, and by referring to their principal chemical and agricultural uses.

Among the many investigations undertaken to solve this problem two directions have led to industrial methods—the one, calcium cyanamide; the other, electrochemical nitric acid.

The principal technical details of the manufacture of calcium cyanamide are given, and it is pointed out that its cost price depends upon that of calcium carbide. From this it is concluded that a kilogram of nitrogen fixed as calcium cyanamide will cost a little more than ammonia salts and Chili saltpetre, if the excess of calcium carbide obtained in carbide works not available for the development of acetylene is used. This conclusion seems confirmed by some agricultural tests made with this new compound of nitrogen of which the value, relative to Chili saltpetre, is not definitely fixed.

Passing to electrochemical nitric acid the author summarises the principles of its preparation, and although these are very simple, the application has presented serious difficulties, which, however, now appear to be solved by the experiments carried out in Norway. The absorption of the nitric acid by sulphuric acid is insisted on, as this allows concentrated nitric acid to be directly obtained, which is of greater commercial value than nitrate of lime, and consequently of more interest to a new industry. Analysis of the cost of electro-chemical nitric acid leads to the conclusion that a kilogram of nitrogen is fixed slightly cheaper as nitric acid than as calcium cyanamide.

In concluding, the author discusses the exterior economic factors which may hasten the development of the nitrogen industries. Among these the direct synthesis of ammonia from nitrogen and hydrogen, and the recovery of the nitrogen of coal in the ammoniacal form by the methods of L. Mond, are mentioned. These processes, combined with the production of electro-chemical nitric acid, will in all probability solve the solution of obtaining electric energy cheaply by motors utilising the power of coal.

THE SIXTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

The Committee responsible for the arrangements made for the Sixth International Congress of Applied Chemistry may congratulate themselves upon having organised a most successful meeting. The Italian Government placed at their disposal the new Palace of Justice, which building offered every advantage for the purposes of such a Congress. On the evening preceding the formal opening by the King and Queen of Italy on April 26th, a pleasant social gathering of the members of the Congress took place at the Hotel Excelsior, on the invitation of the Chemical Society of Rome. The meetings of the sixteen

sections into which the Congress was divided, occupied both the mornings and afternoons from April 26th to May 3rd, while general meetings were held on April 28th to hear Sir William Ramsay's paper dealing with sewage disposal; on the 30th, when Professor Moissan read a highly interesting paper on the distillation of the metals; on May 1st, when Dr. Adolf Frank described his process for the utilisation of the nitrogen of the atmosphere for the preparation of artificial manures; and on May 2nd, when Dr. Otto Witt explained the objects of the Congress and the true meaning of the term "Applied Chemistry." On May 5th, a State banquet was held for the delegates of foreign governments and societies, and a reception by the King at the Quirinal. The Committee had arranged many social gatherings and excursions to places of interest in the neighbourhood, and these were largely attended by the members, who were enthusiastic about the scenic beauties of such places as Tivoli, and the artistic treasures of Rome itself. Circumstances arose to prevent some of the longer excursions to Sicily and Elba. It is no doubt unnecessary to emphasise the fact that the utmost hospitality was extended to the 1800 members of all nationalities who attended the Congress, and that every possible arrangement was made for the comfort and welfare of their guests by the Committee. The seventh meeting is to take place in London in 1909, on the invitation of Professor Tilden, representing the British Government, and of a Joint Committee elected by the members of the various British societies connected with chemistry, and special interest will no doubt be evinced in it, since it will be the first meeting to be held in London.

Among the more important papers read before the Congress may be specially mentioned Sir William Ramsay's excellent account of the purification of sewage water, in which he discussed the different methods now employed for this purpose, laying stress on bacteriological processes.

Professor Moissan's description of his work on the distillation of the metals was also heard with much interest. By means of the electric furnace he has succeeded in distilling copper with great ease, gold being somewhat more refractory than copper, while the platinum metals are still more difficult to distil. The metals of the iron group are vaporised at the temperature of the furnace, and also boron, carbon, titanium, and silicon. Thus the author has now shown that all substances are volatile at about 3500°, and this is therefore the highest limit of the temperature of the sun, which must in reality lie some hundreds of degrees lower than this limit, as most of the elements of which it can be shown by spectral analysis to consist are volatile at a lower temperature.

Sir William Ramsay contributed also a paper on the Bischoff process for manufacturing white lead, which does away with the dust which constitutes a danger to the workpeople. In this process litharge is reduced at about 300° to a black lead suboxide of variable composition, by means of water-gas, prepared by leading a current of water vapour over strongly heated coke. The suboxide is mixed with water till a yellow mixture of oxide and hydroxide is obtained; this is saturated with carbon dioxide and a dilute solution of lead acetate added, the white lead thus obtained being compressed and mixed with oil.

Two papers by C. Nicolardot, read before the Analytical Chemistry Section, describe methods of separating iron from metals and metalloids, which seem likely to find practical application. The process in its simplest form is carried out as follows:—The alloy or ore is first dissolved by means of hydrochloric acid or nitric acid, or a mixture of these acids, the solution is filtered and oxidised with nitric acid or chloric acid. If no volatile chlorides are present the solution is evaporated to dryness, or if aluminium is present it is merely heated to 100°. After standing for some hours it is dissolved, the liquid is neutralised with ammonia if it contained volatile compounds. It is then boiled, ammonium sulphate solution added, and the precipitate which slowly forms is filtered and well washed. If chromium or aluminium is present it

is best to treat the ore with hydrochloric or sulphuric acid, or to fuse with acid potassium sulphate, filter, evaporate to dryness, re-dissolve the residue, and add SO₂ solution; the chromium and aluminium sesquioxides are then separated off, the liquid is neutralised in the cold with ammonia, and ammonium sulphite is added, the solution boiled, and the basic sulphites ignited.

Professor Garelli and Dr. Barbieri in an interesting paper described the preparation of thorium and cerium from monazite sand. The process consists in heating the sand with sodium peroxide, or caustic soda and potassium chlorate, dissolving in sulphuric acid, and treating the solution with ammonia. The precipitate thus obtained is then treated with oxalic acid, and the cerium separated from thorium either with thiosulphate or with salicylic acid.

A paper which was of considerable practical importance was that by Dr. Adolf Frank on the utilisation of the nitrogen of the atmosphere for the production of manures and other nitrogenous substances. Air is first liquefied and fractionally distilled, and thus the nitrogen is separated. This is then heated with calcium carbide, and the calcium cyanamide thus produced may be used directly as a manure. The oxygen obtained as a by-product may be used for the preparation of nitric acid from the ammonia which is also formed from the cyanamide. By means of this process the author has prepared the following substances:—Pure compressed ammonia, ammonium salts, urea, dicyanamide and its salts, salts of dicyandiamine and of guanidine, artificial indigo, &c., so that the great technical importance of Dr. Frank's discovery will at once be recognised.

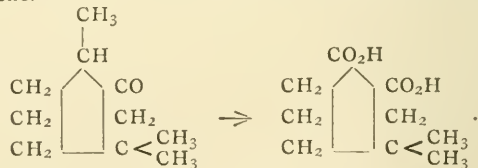
A quick and accurate method of determining albumen in milk was described by Dr. A. Trillat and E. Sauton. The sample of milk (3 c.c.) is diluted with about eight times its volume of water and boiled for five minutes. Five drops of formaldehyde are then added, and the boiling continued for a short time; then the flask is allowed to stand for five minutes, 5 c.c. of 1 per cent acetic acid added, and the whole well shaken. The precipitate is then filtered off, washed with water, freed from fat by digestion in a Soxhlet's apparatus with acetone, dried at 75° to 80°, and weighed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

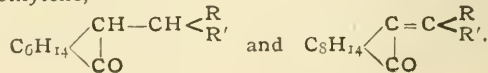
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 18, April 30, 1906.

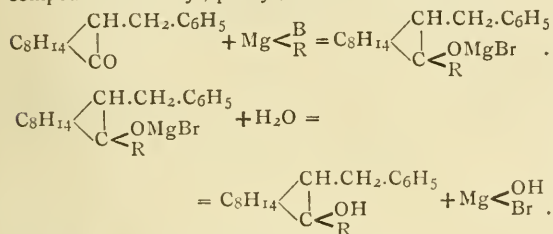
Synthesis of Pimelic ββ-Dimethyl and ββ-Tri-methyl.—G. Blanc.—ββ-Dimethylpimelic acid is of the same importance amongst the terpenic compounds as that of αα- and ββ-dimethylglutaric and adipic acids. It is, in fact, the product of degradation nearest to tetrahydro-eucarvone—a fact which shows the constitution of this ketone.



Diphenyl or Alcoylphenyl Camphomethane and Methylene,—



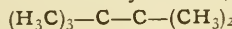
—A Haller and E. Bauer.—The preparation of secondary and tertiary benzylborneols and of the benzylcamphenes, their products of dehydration, led the authors to attempt also the preparation of dibenzyl, phenylbenzyl, and the tertiary alcoylbenzyl borneols. These derivatives are prepared by treating benzylcamphor with organo-magnesium compounds of benzyl, phenyl, and the radicals $C_n H_{2n+1}$.



After preparation, the authors then investigate the properties of the various compounds.

No. 19, May 7, 1906.

Synthesis of Pentamethylethanol,—



—Louis Henry.—

When isobutyric ether, $(H_3C)_2-CH-CO(OC_2H_5)$, acts on magnesium-methyl bromide, $CH_3-Mg-Br$, under advantageous conditions, dimethyl-isopropyl-carbinol, $(H_3C)_2-C(OH)-CH-(CH_3)_2$, is produced. In the same manner, by using ethyl chloroisobutyrate, $(CH_3)_2-CCl-CO(OC_2H_5)$, the chlorohydrine of this alcohol, $(H_3C)_2-CCl-C(OH)-(CH_3)_2$, can be obtained; and from this, under favourable conditions, the author obtains the pentamethylethanol, $(H_3C)_3-C-C(OH)-(CH_3)_2$, which, on oxidation, gives trimethylacetic acid, $(H_3C)_2-CO(OH)$.

Action of Ammonia Gas on Anhydrous Neodymium Chloride.—C. Matignon and R. Trannoy.—At a temperature of 1000° ammonia gas has no action on neodymium chloride. At ordinary temperatures, however, the anhydrous chloride absorbs dry ammonia gas, and during the process increases considerably in volume and acquires a rose tint. A considerable amount of heat is evolved. The authors investigate the compounds thus formed, and show the existence of the following addition compounds:— $NdCl_3 \cdot NH_3$, $NdCl_3 \cdot 2NH_3$, $NdCl_3 \cdot 4NH_3$, $NdCl_3 \cdot 5NH_3$, $NdCl_3 \cdot 8NH_3$, $NdCl_3 \cdot 11NH_3$, $NdCl_3 \cdot 12NH_3$. They also calculate that a total of 147.5 calories are evolved when the ammonia gas unites with one molecule of the chloride.

Existence of Phosphorus Sulphides. Mixtures of Phosphorus and Phosphorus Sesquisulphide.—R. Boulouch.—The author proves the existence of a eutectic in which the concentration of sulphur is 0.335 and the fusion-point exactly -40° . A mixture having the same composition gradually solidifies from $+35^\circ$, and the solid resulting does not constitute a eutectic. The point of eutecty of the mixtures examined is about -7° , and corresponds to a mixture of concentration of 0.200 (P_2S_5 , instead of P_4S_3). The error the author attributes to two causes, which he carefully explains.

Brass.—Léon Guillet.—Industrial brasses which contain more than 55 per cent of copper, and until 63 per cent of copper is present, can be hammered when hot; and when the amount of copper exceeds 60 per cent, they can be hammered and beaten out in the cold. The author investigates certain brasses containing a small percentage of such bodies as aluminium, manganese, silicon, &c., and finds that the presence of foreign elements creates a fictitious standard. The presence of a constituent, in combination or solution, other than that which is recognised in the copper-zinc alloys, considerably diminishes the mechanical value of the alloy.

Estimation of Small Quantities of Iron.—A. Mouneyrat.—If a current of sulphuretted hydrogen passes through a dilute alkaline solution of an iron salt, this solution, independently of the precipitate of sulphide which is formed, turns a deep green. An investigation of this coloration led the author to discover an extremely sensitive reaction for iron, much more sensitive than the sulphocyanide reaction. It is especially useful for the detection of this element in aqueous solutions containing mere traces. The intensity of the green colour of solutions containing between 1, 1,000,000 and 1/1000 part of iron is proportional to the amount of iron present.

Preparation of Aromatic Sulphamates by Reduction of their Nitrated Derivatives with Sodium Hydrosulphite.—A. Seyewetz and M. Bloch.—The aromatic sulphamates of general formula $(R)N.H.SO_3(M)$ have been obtained by various methods. Either a simple or substituted amine or a hydroxylamine are used in the NH_2 or $NHOH$ group, of which the sulphonic group is substituted by means of sulphuric chlorhydrin, amido-sulphuric acid, sulphurous acid, or thionylamine. The authors' method consists in directly transforming the NO_2 group into $NH-SO_3Na$, and thus obtaining the corresponding sulphamate with good yields, owing to the reduction of the nitrated derivatives with sodium hydrosulphite.

MISCELLANEOUS.

Society of Public Analysts.—Owing to the fact that the Anniversary Dinner of the Society takes place on June 13th, the ordinary meeting announced for Wednesday, the 6th inst., was postponed to Thursday, the 14th inst.

Literary Intelligence.—At a time when so much interest is centring around the disclosures at the slaughter-houses of Chicago, the appearance of an authoritative work bearing on the subject is opportune. Messrs. J. and A. Churchill are just about to publish "Preservatives in Food and Food Examination," by Dr. John C. Thresh, Lecturer on Public Health at the London Hospital Medical College, and Medical Officer of Health for Essex, and Dr. Arthur E. Porter, Assistant Medical Officer of Health and Chief Sanitary Inspector, City of Leeds. In this work of 500 pages a critical examination is made of the various preservatives used in beverages and foods, while the question of unsound food is fully discussed. The authors maintain that "during recent years it has become notorious that serious and widespread epidemics of illness are attributable to the use of food which has become infested with organisms capable of producing disease." The text is elucidated by well executed plates.

Oxidation of Nitrous Acid by Hydrogen Peroxide. **Determination of Nitrate in presence of Nitrite.**—M. Busch.—Hydrogen peroxide is a convenient reagent to oxidise nitrous acid quantitatively to nitric acid. The reaction, $HNO_2 + H_2O_2 = HNO_3 + H_2O$, occurs very rapidly in acid solution at a temperature of 60° to 70° . If to a liquid containing a nitrite excess of neutral hydrogen peroxide solution is added, the whole warmed to 70° , and acidified with very dilute sulphuric acid, no nitrous fumes escape, and no trace of nitrous acid remains when the reaction is completed. When both acids are present the HNO_3 is best estimated gravimetrically by means of nitron acetate solution. In one half of the solution the nitrous acid is determined volumetrically by means of permanganate and the other half is oxidised with hydrogen peroxide, and then the total quantity of the two acids is weighed as nitron nitrate. The difference gives the nitric acid present. The simplest way is to precipitate with nitron acetate the liquid obtained after the titration with potassium permanganate. (Nitron = diphenyl-*endo*-dihydrotriazole; see article by M. Busch on "Gravimetric Estimation of Nitric Acid," *Berichte*, 1905, xxxviii., 861,

abstracted in CHEMICAL NEWS, 1905, xci., 234).—*Berichte*, xxxix., No. 6.

Hexamethylethane: a New Octane,

(H_3C)₃—C—C—(CH_3)₃.—Louis Henry.—This interesting hydrocarbon is formed as a by-product in the synthetic preparation of pinacolic alcohol, (H_3C)₃—C—CH(OH)—CH₃, when acetic aldehyde, H_3C —CHO, acts on a mixture of magnesium with tertiary butyl bromide, (H_3C)₃—CBr. The hexamethylethane formed is a crystalline white solid with penetrating odour. It volatilises and rapidly disappears in free air. It melts at 103–104° in a closed capillary tube, and boils at 106–107° under 765 m.m. pressure. Its vapour density is 3.93. This hydrocarbon completes the series of the double symmetric methylation of ethane.—*Comptes Rendus*, cxlii., No. 20.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Amorphous Elements and Liquid Air.—Will any reader kindly give particulars where I may obtain information as to any marked change in the amorphous forms of the non-metallic elements when subjected to intense cold, as in that of liquid air. I am under the impression that the waxy variety of phosphorus is converted into the red variety, exceedingly liable to most violent explosion. Is there a corresponding alteration in specific gravity? Does the crystalline variety of phosphorus undergo any marked change under similar conditions?—G. W. C.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Royal Institution, 5. General Monthly Meeting.
Society of Chemical Industry, 8. "Recent Progress in the Cement Industry," by Bertram Blount.
"Purifying and Stabilising Guncotton," by R. Robertson.

THURSDAY, 14th.—Society of Public Analysts, 8. (Postponed from the 6th inst.).

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THE CHEMICAL NEWS.

VOL. XCIII., No. 2429.

ON THE ATTACK OF PLATINUM BY SULPHURIC ACID.*

By M. QUENNESSEN.

THE action of sulphuric acid on platinum has given rise to many memoirs, among the most important of which we may mention those of Scheurer-Kestner (*Comptes Rendus*, 1878, lxxxvi., 1082; 1880, xci., 59; *Bull. Soc. Chim.*, 1875, [2], xxiv., 501; 1878, xxx., 28) and Conroy (*Journ. Soc. Chem. Ind.*, 1903, xxii., 465). The first states that the presence of nitrous products hastens the solution of platinum in sulphuric acid; the second, on the contrary, attributes to them a retarding action.

Quite recently M. Delépine (*Comptes Rendus*, 1905, cxli., 866, 1013; *CHEMICAL NEWS*, 1906, xciii., 108) has recorded a much stronger attack of the metal than is shown by the figures given by Scheurer-Kestner; moreover, according to his observations the addition of nitric acid to the sulphuric acid has no influence on the rapidity of the attack.

The question did not appear to me to be nearer solution than it was before, and I therefore undertook with pure sulphuric acid a few researches which have thrown new light on this problem, so important in the large chemical industries.

After having ascertained by the ferrous sulphate and the diphenylamine methods that the sulphuric acid employed was quite free from nitrous compounds, I first studied the action of acid containing 94 per cent SO_4H_2 on commercial platinum. With this object I took metal serving for the manufacture of the vessels used for concentrating this acid, and I purposely exaggerated the temperature by going far beyond the maximum of 280° attained in industry for obtaining acid of 94 per cent monohydrate. Finally, I repeated the same experiments with pure platinum specially prepared for this purpose. Also, to avoid any action of the acid sulphate of potassium employed by M. Delépine to raise the point of ebullition, I operated in a sealed tube between 390° and 400° . Sainte-Claire Deville, moreover, showed that this salt attacks platinum at the level of the air zone.

The results of these experiments, all of which had a duration of nine hours at 400° , are given by reducing the attack to a square decimetre of metal during one hour (50 c.m.² on each side).

With commercial platinum the heating was effected—(1) in a vacuum, and (2) in an atmosphere of oxygen.

In a vacuum the metal dissolved was 0.001 grm. per decimetre-hour, and in oxygen it was 0.124 grm. In the second experiment, on opening the tube I found there was a partial vacuum, corresponding to 35 m.m. of mercury for the volume of the tube employed. There therefore was an absorption of oxygen.

With pure platinum in the same conditions the results were as follows:—

In the tube filled with oxygen the attack was not more than 0.0227 grm. per decimetre-hour, and in that *in vacuo* it was 0.0006 grm.

In these four experiments the sheets of metal were rolled in a spiral form; I therefore was able to see that only those parts immersed in the acid were attacked, the surfaces out of the liquid having preserved their brilliancy.

Commercial platinum is strongly etched (*moiré*), while the pure metal is only brightened.

Having established these facts I have continued the

experiments exclusively with pure platinum, in presence of acid of different degrees of concentration and only in a vacuum, the intervention of oxygen having been clearly established by the first experiments.

With acid, SO_4H_2 , containing about 2 per cent excess of anhydride, the attack was 0.0265 grm. per decimetre-hour, practically the same as that of pure metal in oxygen, and on opening the tube I observed the decided presence of sulphurous acid, which I also noticed in the following two experiments.

With an acid of 98.6 per cent of SO_4H_2 the attack was 0.0076 grm. per decimetre-hour, while with acid of 96.75 per cent the loss was only 0.0014 grm. In this latter experiment the temperature accidentally rose to 450° for one hour.

To sum up, I conclude that in the first instance, with an acid such as is prepared for commercial use, it is the atmospheric oxygen which acts as an oxidising agent, while with sulphuric acid of greater strength, in the absence of free oxygen, it is the sulphuric anhydride in solution in sulphuric acid which furnishes the oxygen necessary for oxidation, in accordance with a phenomenon of the same character as that which serves for the preparation of sulphurous acids with the common metals. The mechanism will be understood by reference to the work of Dittmar (*Journ. Chem. Soc.*, 1869, [2], vii., p. 446) on the dissociation of SO_4H_2 into $\text{SO}_3 + \text{H}_2\text{O}$ in sulphuric acids of unusual strength.

INVESTIGATIONS ON THE OCCURRENCE OF CHANGES IN THE TOTAL WEIGHT OF SUBSTANCES UNDERGOING CHEMICAL TRANSPOSITIONS.*

(SECOND COMMUNICATION).

By H. LANDOLT.

In the year 1893 I published in the *Sitzungsber.*, pp. 301–334, an experimental article on the question whether in chemical transpositions the total weight of the substances taking part in the reaction remains absolutely unaltered, or whether small variations can be detected. We can conceive of the possibility of the latter alternative if we suppose either that gravity does not act with exactly the same intensity upon different substances, or that the total mass suffers an increase or decrease. The latter supposition could be explained by an hypothesis put forward by Lothar Meyer, according to which, besides the particles of the material, the ether also enters into the composition of the chemical atom, and is perhaps not absolutely imponderable; the amount of it may possibly alter during the reaction, and it may be able to pass through the walls of the vessel.

The experiments extended to reactions which occur in aqueous solution. The substances were introduced separately into the two limbs of a glass vessel shaped thus, Π ; the open ends of the vessel were then fused up, two such pieces of apparatus (A and B) of almost equal weight and of the same external volume being prepared and placed upon the two scale pans of the balance. The difference of weight of these two vessels was then determined—(1) in the original condition, (2) after the reaction had taken place in apparatus A, (3) after the reaction had taken place in B, by which each experiment was performed twice.

The investigation included the following transpositions, the substance named second being always present in excess:—

1. $\text{Ag}_2\text{SO}_4 + 2\text{FeSO}_4 = 2\text{Ag} + \text{Fe}_2(\text{SO}_4)_3$.
2. $\text{HIO}_3 + 5\text{HI} = 6\text{I} + 3\text{H}_2\text{O}$.
3. $2\text{I} + 2\text{Na}_2\text{SO}_3 = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$.
4. $\text{C}_2\text{Cl}_3\text{H}_3\text{O}_2 + \text{KOH} = \text{CHCl}_3 + \text{CHKO}_2 + \text{H}_2\text{O}$.
5. $\text{C}_2\text{Cl}_3\text{H}_3\text{O}_2 + \text{water (solution process)}$.

* Communicated by the Author, being a Paper presented to the Académie des Sciences.

* From *Sitzungsber. d. K. Akademie d. Wissensch.*, 1906, viii., 266.

In Table I., Col. I. contains the details of the quantities of the substances taking part in the reactions; Col. IV. the observed alteration in weight in m.grms.; Col. V. the mean error affecting the weighing.*

TABLE I.

I.	II.	III.	IV.	V.
Mass of Reagents.	No.	Vessel.	Observed alteration in weight.	Error in weighing.
Grms.			M.grms.	M.grms.
REACTION I.—Silver Sulphate and Ferrous Sulphate.				
Silver separated	30	1 A	-0.0167	± 0.021
		2 B	-0.0131	0.030
	60	3 B	-0.0130	0.017
REACTION II.—Iodic Acid and Hydriodic Acid.				
Iodine separated	64.9	4 A	-0.0047	± 0.022
		5 B	-0.0114	0.013
		6 A	-0.0103	0.022
	80.0	7 B	-0.0102	0.016
		8 A	-0.0177	0.012
	160.0	9 B	-0.0111	0.013
REACTION III.—Iodine and Sodium Sulphite.				
Iodine used up	90	10 A	+0.0105	± 0.008
		11 B	-0.0031	0.017
		12 A	+0.0002	0.020
	110	13 B	-0.0127	0.017
REACTION IV.—Chloral Hydrate and Potassium Hydroxide.				
Chloral hydrate	150	14 A	+0.0012	± 0.024
used		15 B	+0.0007	—
REACTION V.—Chloral Hydrate and Water.				
Chloral hydrate	312			
Water	104	16 A	-0.0003	± 0.013

As may be seen from Table I., in the first two reactions alterations in weight occurred, in amounts which mostly greatly exceeded the errors in weighing. But as it had appeared that, firstly, of the six experiments with iodic and hydriodic acids two (Nos. 4 and 9) gave hardly any change, and, secondly, in the reaction between iodine and sodium sulphite (Nos. 10 to 13) both positive and negative numbers occurred, and finally no definite proportionality between the reaction mass and the alteration of weight could be detected, it still seemed conceivable that experimental errors of an external kind had prevented perfect constancy of weight. I therefore stated that the variations had not been definitely proved, but at the end of the paper I added that it would be interesting to examine the repeated decreases of weight which had been found when silver and iodine were reduced to see if they always occurred in a series of further experiments, because at any rate it was not perfectly certain that they were all due to errors of observation.

As regards the above experimental results, R. v. Lieben (*Physikalische Zeitschrift von Riecke und Simon.*, 1900, I., 237) suggested that they might possibly be connected with the alterations in the dissociation proportions occurring in the reactions, or to the appearance or disappearance of electrons. After it had already been shown in another way (cathode rays) that they have a definite mass, it was clear that decreases of weight must take place in the transposition II. mentioned in the table, as well as in I., where a repression of the total dissociation occurs, and, on the contrary, increases in III., as was observed in Experiment 10. The processes IV. and V., on account of the exceedingly small dissociation, would lead us to expect no alteration in weight, which agrees with the observations. With regard to this hypothesis, it may be remarked that the experiments subsequently performed by Heydweiller

and by me, which gave a decrease instead of the expected increase when salts dissolved, are not in harmony with it.

Experiments of Other Observers.

As was mentioned in the first paper, in 1891 Kreichgauer, of Berlin, investigated whether, in the chemical union of mercury with bromine or iodine in a closed vessel, the total weight is altered, and he thus obtained only very small differences. After the appearance of my paper the subject was at once taken up by a number of other observers, among whom are the following:—

(a) F. Sanford and L. E. Ray (*Physical Review*, 1897 v., 247) examined the reaction between ammoniacal solution of silver nitrate and grape-sugar, using the method applied by me, but not weighing so accurately. When about 60 grms. of silver were reduced five experiments gave the numbers:—

Expt. No.	Observed alteration in weight.	Probable error in weighing.
	M.grm.	M.grm.
1.	-0.05	± 0.07
2.	-0.05	± 0.05
3.	-0.03	± 0.07
4.	+0.04	± 0.04
5.	+0.08	± 0.04

Thus, both positive and negative differences appear and of the same order of magnitude as the errors in weighing.

(b) In 1901, A. Heydweiller (*Drude's Ann. d. Physik.*, 1901, v., 394; Prelimin. Comm. in the *Physikal. Zeitschrift*, 1900, I., 527) published an exhaustive article on alterations in weight during chemical and physical changes. The experiments were performed with two β -tubes, and every precaution was taken. A difference from my method lay in the fact that the vessels were not made of equal volume by the addition of substances, but their difference of volume was determined, and the unequal upward pressure in weighing was corrected by determining the density of the air. The weight of an apparatus when prepared amounted to about 300 grms., and that of the substances used + water to about 200 grms. The probable error of the mean value of the weighings, according to Heydweiller, amounted to ± 0.01 m.grm., and he assumed that alterations in weight, which exceeded 0.04 m.grm., could not be ascribed to experimental errors.

The experiments given in Table II. were performed. As appears at once from the table there is a great preponderance of negative signs, and thus the results resemble mine, which also gave decreases for the most part. As regards the separate processes we notice:—

I. The reaction between Fe and CuSO_4 proceeded without appreciable alteration of weight, if the copper vitriol used was free from acid (Expts. 1 and 2); on the other hand, a decrease far exceeding the experimental error (0.04 m.grm.) occurred if the solution contained only a very small quantity of alkali (Expts. 3, 4, and 5), or sulphuric acid (Expts. 6 and 7). The action of these substances is obscure.

II. On dissolving copper vitriol free from acid in water again hardly any decrease occurred (Expt. 8), but there was a very large decrease when ordinary salt was used (Expt. 9), or when sulphuric acid was added (Expts. 10 and 11).

III. On mixing copper sulphate solution with dilute sulphuric acid no alteration of weight took place (Expt. 12).

IV. The decomposition of copper sulphate with caustic potash (Expts. 13 to 18) was always accompanied by a decrease of weight, which, on partial mixing of the liquids, is smaller than on complete mixing (Expts. 13, 14, and 16, 17).

V. The small alterations of weight which appeared on neutralising acetic acid with ammonia (Expts. 19 and 20) are within the limits of experimental error (0.04 m.grm.).

VI. The same holds good when barium chloride is decomposed by sulphuric acid.

* In the former paper the error given was the probable and not the mean, the first of which amounts to two-thirds of the second.

TABLE II.

Expt. No.	Contents of the two limbs of the vessels.	Observed alteration in weight.
I. Iron and Copper Sulphate.		
<i>a. Solution Neutral.</i>		
1.	13.96 grms. Fe; 63.8 grms. $\text{CuSO}_4 \cdot 5 \text{ aq}$ + 100 grms. water	M.grms. -0.026
2.	13.96 grms. Fe; 63.1 grms. $\text{CuSO}_4 \cdot 5 \text{ aq}$ + 100 grms. water	+0.019
<i>b. Solution Alkaline.</i>		
3.	15 grms. Fe; 79.9 grms. $\text{CuSO}_4 \cdot 5 \text{ aq}$ + 130 grms. water with trace of NaOH	-0.217
4.	15 grms. Fe; 69.6 grms. $\text{CuSO}_4 \cdot 5 \text{ aq}$ + 115 grms. water with 0.13 gm. NaOH	-0.161
5.	18.3 grms. Fe; 98.0 grms. $\text{CuSO}_4 \cdot 5 \text{ aq}$ + 103 grms. water with 0.23 gm. NaOH	-0.176
<i>c. Solution Acid.</i>		
6.	15 grms. Fe; 69.6 grms. $\text{CuSO}_4 \cdot 5 \text{ aq}$ + 114.2 grms. water with 0.36 gm. H_2SO_4	-0.097
7.	18.3 grms. Fe; 103.2 grms. $\text{CuSO}_4 \cdot 5 \text{ aq}$ + 92 grms. water with 0.06 gm. H_2SO_4	-0.158
II. Solution of Copper Vitriol in Water.		
8.	62 grms. salt crystallised from alkaline solution; 151 grms. water	-0.029
9.	62 grms. ordinary copper vitriol; 147 grms. water	-0.126
10.	50 grms. ordinary salt; 150 grms. water containing 7.3 grms. H_2SO_4	-0.081
11.	50 grms. ordinary salt; 150 grms. water containing 3.7 grms. H_2SO_4	-0.072
III. Mixture of Copper Sulphate Solution with Dilute Sulphuric Acid.		
12.	38 grms. $\text{CuSO}_4 \cdot 5 \text{ aq}$ + 110 grms. water; 2.37 grms. H_2SO_4 + 10 grms. water..	+0.014
IV. Mixture of Copper Sulphate Solution with Caustic Potash.		
(38 grms. $\text{CuSO}_4 \cdot 5 \text{ aq}$ + 110 grms. water; 2.25 grms. KOH + 10 grms. water).		
13.	After addition of half the caustic potash ..	-0.037
14.	After addition of all the caustic potash ..	-0.092
(33 grms. $\text{CuSO}_4 \cdot 5 \text{ aq}$ + 92 grms. water; 10.04 grms. KOH + 40 grms. water).		
15.	After complete mixing in Vessel A ..	-0.068
16.	After half mixing in Vessel B ..	-0.059
17.	After complete mixing in Vessel B ..	-0.080
18.	34.4 grms. $\text{CuSO}_4 \cdot 5 \text{ aq}$ + 99.5 grms. water; 13.4 grms. KOH + 15 grms. water	-0.045
V. Acetic Acid and Ammonia.		
19.	49.7 grms. $\text{C}_2\text{H}_4\text{O}_2$ + 87.5 grms. water; 15.3 grms. NH_3 + 123.7 grms. water ..	-0.034
20.	50.4 grms. $\text{C}_2\text{H}_4\text{O}_2$ + 88.5 grms. water; 15.6 grms. NH_3 + 125.9 grms. water ..	-0.026
VI. Barium Chloride and Sulphuric Acid.		
21.	20.0 grms. BaCl_2 + 100 grms. water; 9.7 grms. H_2SO_4 + 40.3 grms. water ..	-0.016

As Heydweiller emphasises, no connection can be observed between the alterations in weight, and the other physical and chemical processes occurring during the reaction, they appear both with increases (Group II.) and decreases (IV. and VI.) of the electrolytic dissociation, density (II. and VI.), and magnetic permeability (I.).

With regard to Heydweiller's experiments, Lord Rayleigh (*Nature*, 1901, lxiv., 181) remarked that there was not

always a state of equilibrium in the vessels before the transposition, as, for example, in Group II., when solid copper vitriol was in one limb and water in the other. By continuous distillation of the water, changes of temperature might be caused, and they would possibly influence the determination of the weights. In a rejoinder of Heydweiller's (*Physikal. Zeitschrift*, 1902, iii., 425) he points out that if this were the cause of the decreases of weight observed in Experiments 9 to 11, the action would also have manifested itself in Experiment 8, where, however, practically no alteration appeared.

(c) In 1903, J. Joly ("On the Conservation of Mass," *Royal Dublin Soc. Trans.*, 1903, Ser. 2, viii., 23—52), of Dublin, in quite a different way, investigated whether, on dissolving copper vitriol in water, any change of mass could be observed. Stated shortly, the method consisted in hanging on one end of a torsion balance a glass vessel containing the two substances at first separated, and when at mid-day or midnight the arms were perpendicular to the direction of the earth's motion, the salt was allowed to dissolve. Acceleration would be obliged to occur if mass disappeared, and conversely. Of fourteen observations eight argued definitely and three less clearly for a decrease of mass, two were against it, and the last was doubtful.

(d) In 1903, G. Kahlbaum performed experiments on the question whether, when the grey modification of tin is converted into the white, and *vice versa*, any change of weight can be observed. The weighings showed no such change.

(e) In 1904, A. Lo Surdo (*Nuovo Cimento*, 1904, Ser. 5, viii.), of Messina, investigated very carefully the reaction between iron and copper sulphate. He used η -shaped vessels of Thuringian glass, which, as in Heydweiller's experiments, contained on the one side about 15 grms. of iron powder, and on the other about 80 grms. of copper sulphate and 200 to 250 grms. of water to which a small quantity of caustic soda had been added. The external volume of the apparatus, adjusted to 0.004 to 0.023 c.c. by addition bodies, was determined before and after the reaction, when the alterations denoted below by *b* were observed. The weighings were performed with a balance fitted with mirror reading arrangement from Sartorius, of Göttingen (sensitivity, 20 to 30 scale divisions per m.grm.). The balance possessed an arrangement by which the vessels could not only be exchanged but also inclined, so that the reaction could be carried out within the balance case without touching the glass. The probable error of the mean of six or seven single weighings amounted to ± 0.003 m.grm. to ± 0.007 m.grm., and in one case to ± 0.012 m.grm.

Five weighings gave the following results:—

Expt. No.	a. Change of weight. M.grm.	b. Change of volume. C.c.
1.	+0.008	+0.011
2.	-0.008	+0.002
3.	-0.008	+0.008
4.	+0.013	+0.003
5.	+0.003	-0.006

As the experimental errors are estimated at 0.02 m.grm. at the most the alterations of weight lie completely within this limit, and they would not differ appreciably if corrections for change of volume were applied. Hence, Lo Surdo concluded that during chemical reactions no perceptible differences of the total weight can be observed.

But it must be noted that this statement applies only to the reaction between iron and copper sulphate.

In view of the contradictory results obtained by the various workers, a fresh investigation of the problem was an urgent necessity. It had to be decided definitely whether the decreases of weight found repeatedly by Heydweiller and myself for several reactions were caused only by experimental errors, produced by purely external causes of little interest, or whether they were connected with the alteration of the substances.

As according to previous experience* the effect of any inequality of gravity upon different bodies is infinitely small, from the axiom of the conservation of matter, the cause of the observed decreases of weight can be sought only in a decrease of mass. In my first paper I took into consideration the presence of ether, either contained in the atoms (Lothar Meyer) or strongly condensed round them (C. Nägeli), and partially escaping during the reaction. Also Lieben's view, that the alterations in weight were possibly connected with the appearance or disappearance of electrons, was mentioned. Moreover, in the present age of radio-activity, when the spontaneous alterability of the atoms of several elements has been recognised, the conjecture may be expressed, that in consequence of the violent shock which the atoms suffer in chemical reactions, both radio-active and other elements may have a small part of their mass split off. If it is possible that the released particles on account of their minuteness can pass through the walls of the vessel, in chemical transpositions decreases of weight would appear, but no increases.

When I resolved to take up the subject again, the earlier experiences, acquired in the years 1890-1892, led me to expect a very lengthy and tedious piece of work. It had been found that the alterations of weight which occurred never exceeded 0.17 m.grm., and mostly amounted to hundredths of a m.grm., a region in which the weighing of glass vessels might be affected by many sources of error. The only hope of obtaining more certain results lay in considerably increasing the accuracy of the method, and especially of the weighing. Luckily this was made possible owing to the exceedingly acceptable assistance of the Akademie der Wissenschaften and of the Kgl. Cultusministerium, through whom I obtained possession of a new and excellent balance, besides other necessary instruments. A beginning was made with the experiments at the end of the year 1901; they gave almost always decreases of weight in different reactions, but there was still often a doubt whether they were not to be ascribed to external influences. I could not feel confidence in the results till an extended series of experiments had been finished in which the vessels were filled with substances not capable of reacting with one another, and then treated in exactly the same way as in the experiments with substances which underwent chemical transposition. Under these circumstances decreases and increases of weight occurred in almost equal numbers, and were, moreover, very considerably smaller than those occurring during the reactions. As will be explained in full later, the greatest error which affected the whole method, including the weighing, was proved to be ± 0.03 m.grm.

In this communication I must limit myself to a statement of the results and a short description of the methods. The material used for the observations was very extensive, and I have therefore been obliged to prepare another complete report of the whole work, which I shall present for the *Transactions* of the Akademie.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 11th instant, the Rt. Hon. Sir James Stirling, Vice-President, in the Chair. Mrs. Elgar, Miss Hilda Hanbury, Mr. E. L. Mansergh, Mrs. Morse, and Mr. C. D. Page were elected Members. The Special Thanks of the Members were returned to Sir Andrew Noble, K.C.B., F.R.S., for his donation of £100, and to Mrs. Frank Lawson for her donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures.

* According to the observations of R. von Eötvös and D. Reichgauer mentioned in the first paper, it is to be assumed that if, generally speaking, there is a difference in the weight of bodies of the same mass, but of different material, this amounts to less than a twenty millionth part of the measured magnitude. For a reacting mass of 100 to 200 grms. as was used in the experiments here referred to, the difference would amount to 0.005 to 0.010 m.grm., and would thus lie within the limits of experimental error.

THE BEARING OF HYDRATES ON THE TEMPERATURE COEFFICIENTS OF CONDUCTIVITY OF AQUEOUS SOLUTIONS.

By HARRY C. JONES.

THAT the electrical conductivity of aqueous solutions of electrolytes, in general, increases greatly with rise in temperature is a well known fact. This might be due either to an increase in the dissociation of the electrolyte with rise in temperature, or to an increase in the velocity with which the ions move, or to both. It is not a difficult matter to test the effect of change in temperature on the dissociation of electrolytes. It is only necessary to measure the dissociation directly, at different temperatures, by the conductivity method. This has been done recently by Jones and West (*Am. Chem. Journ.*, 1905, xxiv., 357), for temperatures ranging from 0° to 35°. The result is that electrolytes, in general, are *slightly* less dissociated at the higher than at the lower temperatures.

As has been pointed out, this is in accord with the theory of Dutoit and Aston, which makes the dissociating power of a solvent a function of its own association—the more associated a solvent the greater its dissociating power. Take a solvent like water, the higher the temperature the less it is associated, and, consequently, the smaller its power to break molecules of electrolytes down into ions.

Having eliminated the factor of dissociation as increasing the conductivity of electrolytes at the higher temperature, we are forced to conclude that the increase in conductivity with rise in temperature, shown by solutions of electrolytes in general, is due to an increase in the velocities with which the ions move.

There are a number of factors which determine the velocity with which an ion moves through a solution of an electrolyte. Assuming that the force which drives the ions is constant, *the velocity would be conditioned chiefly by the viscosity of the medium through which the ion passed, and by the size of the ion.* At the more elevated temperature the force which drives the ion would be greater, and the viscosity of the medium through which the ion moves would be less. Both of these factors would increase the velocity with which the ions move, and, consequently, increase the conductivity as the temperature was raised.

The object of this paper is to call attention to another factor which causes the ions to move faster at the more elevated temperature. *The mass of the ion decreases with rise in temperature.* This does not refer to the charged atom or group of atoms which we usually term the ion, but to this charged nucleus plus a larger or smaller number of molecules of water which are attached to it, and which it must drag along with it in its motion through the remainder of the solvent.

That ions are hydrated has been shown beyond question by Jones and his co-workers. That these hydrates are relatively unstable compounds has also been demonstrated; the higher the temperature the less complex the hydrates existing in the solution. This can be seen from one example. In a solution of a certain definite concentration, every molecule of calcium chloride or the ions resulting from it holds about 30 molecules of water. From such a solution practically all of the water can be removed by simply boiling it, except 6 molecules of water to 1 of calcium chloride—this number being brought out of the solution by the salt as water of crystallisation. The higher the temperature, then, the less complex the hydrate formed by the ion. The less the number of molecules of water combined with the ion the smaller the mass of the ion, and the less its resistance when moving through the solvent. Consequently, the ion will move faster at the high temperature. This conclusion can be tested by the results of experiment. If this factor of diminishing complexity of the hydrate formed by the ion with rise in temperature, plays any prominent rôle in determining the large tem-

perature coefficient of conductivity, then we should expect to find those ions with the largest hydrating power having the largest temperature coefficients of conductivity. This will readily be seen to be the case. The more complex the hydrate, *i.e.*, the greater the number of molecules of water combined with an ion, the greater the change in the complexity of the hydrate with rise in temperature. We can readily test this conclusion by the results of the experimental work of Jones and West (*Am. Chem. Journ.*, 1905, xxxiv., 357). Let us compare the temperature coefficients of conductivity per degree rise in temperature, for some of those substances which have slight hydrating power, with the corresponding coefficients for a few of the substances which have a much greater power to combine with water.

The volumes for which the comparisons are made range from 2 to 1024, and the temperatures from 25° to 35°.

A comparison of Table I. and Table II. will show that the above conclusion is confirmed by the experimental results. The substances included in Table I. have very slight hydrating power. Those in Table II. have very much greater hydrating power. It will be remembered that hydrating power is a function of water of crystallisation—the larger the number of molecules of water of crystallisation the greater, in general, is the hydrating power of the substance. It will be seen that the substances in Table I. have little or no water of crystallisation, while those in Table II. crystallise with large amounts of water. The water of crystallisation may be taken as roughly proportional to the hydrating power of the substance.

The substances in Table I. have much smaller coefficients of conductivity than those in Table II., even taking into account the fact that those in Table II. are ternary electrolytes, while those in Table I. are binary electrolytes.

TABLE I.—Substances with Slight Hydrating Power.

Temperature coefficients in conductivity units.

	$v=2.$	$v=1024.$
Ammonium chloride ..	2.07	2.94
Ammonium bromide ..	2.16	2.86
Potassium chloride..	2.13	2.84
Potassium bromide..	2.18	2.91
Potassium iodide ..	2.09	2.91
Potassium nitrate ..	1.86	2.71

TABLE II.—Substances with Large Hydrating Power.

Calcium chloride ..	3.11	5.61
Calcium bromide ..	3.01	5.20
Strontium bromide..	2.93	5.27
Barium chloride ..	2.86	5.30
Magnesium chloride ..	2.55	4.59
Manganese chloride ..	2.37	4.86
Manganese nitrate ..	2.24	4.16
Cobalt chloride ..	2.54	4.95
Cobalt nitrate ..	2.48	4.67
Nickel chloride ..	2.63	5.04
Nickel nitrate ..	2.51	4.58
Copper chloride ..	2.15	5.04
Copper nitrate..	2.38	4.88

Another fact, of equal importance, is brought out by comparing the results in Table I. with one another, and similarly those in Table II. with one another. If the temperature coefficient of conductivity is a function of the decrease in the complexity of the hydrate formed by the ion, with rise in temperature, then we should expect that those substances which have equal hydrating power would have approximately the same temperature coefficients of conductivity.

If we examine the above tables we shall see that this is true. The substances in Table I. all have only very slight hydrating power, as would be expected from the fact that they all crystallise without water. Their temperature coefficients of conductivity are all of the same order of magnitude, and, indeed, are very nearly equal.

The substances in Table II. all have very great hydrating power, and all have a hydrating power of the same order of magnitude. This would be expected, since nearly all of these substances crystallise with 6 molecules of water. There are a few compounds in this table calling for special comment. Barium chloride crystallises with only 2 molecules of water, yet it forms hydrates comparable with those substances with larger amounts of water of crystallisation. It is therefore perfectly in keeping with the above relation that its temperature coefficients of conductivity should be of the order of magnitude that they are in the above table.

Manganese chloride crystallises with only 4 molecules of water, but the work of Jones and Bassett (*Am. Chem. Journ.*, 1905, xxxiii., 562) shows that it forms hydrates about as complex as the other salts in Table II. Its temperature coefficients of conductivity are of the same order of magnitude as the other substances in this table.

Of the compounds recorded in Table II., the one which, apparently, presents the most pronounced exception to the relation that we are now considering, is copper chloride. This salt crystallises with only 2 molecules of water, and yet has a temperature coefficient of conductivity that is nearly as large as the salts with 6 molecules of water of crystallisation. It might be inferred that this salt has much less hydrating power than the others in Table II. The work of Jones and Bassett shows that this is not the case (*Am. Chem. Journ.*, 1905, xxxiii., 577). Copper chloride has a large hydrating power, indeed much larger than would be expected from the amount of water with which it crystallises. Its temperature coefficient of conductivity is therefore not surprisingly great.

A third point that is brought out by the results in the above tables is the following:—At the higher dilution the temperature coefficient of conductivity for any given substance is greater than at the lower dilution. That this is a general relation will be seen by reference to the work of Jones and West (*Am. Chem. Journ.*, 1905, xxxiv., 357). This is explained very satisfactorily on the basis of the suggestion made in this paper. The complexity of the hydrate at the higher dilution is greater than at the lower dilution, as is shown by the experiments of Jones and his co-workers on the composition of the hydrates formed by different substances at different dilutions (*Am. Chem. Journ.*, 1905, xxxiii., 534; 1905, xxxiv., 290).

The hydrate being more complex at the higher dilution, the change in the composition of the hydrate with change in temperature would be greater at the higher dilution, and, consequently, the temperature coefficient of conductivity is greater the more dilute the solution.

The three points that are established in this paper are:—

1. The temperature coefficients of conductivity of aqueous solutions of electrolytes are greater, the greater the hydrating power of the electrolyte.

2. The temperature coefficients of conductivity of aqueous solutions of electrolytes are of the same order of magnitude for those substances having, approximately, the same hydrating power.

3. The temperature coefficients of conductivity, for any given substance, increase with the dilution of the solution, and this increase is greatest for those substances with large hydrating power.

All three of these conclusions are necessary consequences of the assumption that the large change in conductivity with change in temperature is due, in part, to the decreasing complexity of the hydrates formed around the ions, with rise in temperature. Since these conclusions are all verified by the results of experiment, we must accept the assumption which led to them as containing a large element of truth.

It is more than probable that the decreasing complexity of the hydrates, with rise in temperature, is a very important factor in conditioning the large temperature coefficients of conductivity, especially of those substances which have large hydrating power.—*American Chemical Journal*, xxxv., No. 5.

A REVISION OF THE ATOMIC WEIGHTS OF
SODIUM AND CHLORINE.*By THEODORE WILLIAM RICHARDS
and
ROGER CLARK WELLS.

(Continued from p. 262).

THE FUSION OF SODIC CHLORIDE IN VACUUM.

THIS matter has been given an especial heading because it is one which has never before received adequate treatment in an investigation of this kind. It is well known that many substances, when fused in the air, dissolve either oxygen or nitrogen, or both, thereby increasing sensibly their weight. While it was hardly to be expected that this would be the case with sodic chloride, the point should not pass unchallenged in a research striving to attain the highest possible accuracy.

Hence two analyses were made of sodic chloride fused for some time in a platinum boat inclosed in a completely evacuated porcelain tube, and subsequently bottled in dry air in the often-described "bottling apparatus." So far as we know, these are the only quantitative experiments ever made in which *all* the weighed substances were fused in a vacuum before weighing. It is true that Stas has shown that ammoniac chloride sublimed in a vacuum gave the same equivalent referred to the silver as preparations sublimed in air; but this choice of ammoniac chloride had the disadvantage that its two dissociation products possess different rates of diffusion, and, moreover, his silver had not been fused in a vacuum as ours had been. The data and results are given below.

The Ratio of Sodic Chloride to Silver.
(Both substances fused in a vacuum).

No.	Sample salt.	Sample Ag.	Weight NaCl. (In vac.).	Weight purest corrected Ag (In vac.).	Parts NaCl equivalent to 100,000 parts Ag.
59.	J	P	3.38684	6.25046	54.185
60.	J	P	4.68529	8.64634	54.188
Average					54.187

These experiments show that probably not enough gas is absorbed during fusion of the salt in air sensibly to alter the apparent combining weight. It is true that gases easily remain in supersaturated solution in liquids, and that long-continued relief from pressure is necessary to remove them; but fused sodic chloride is so mobile and possesses so low a density as to make the retention of much gas very unlikely. That air may be adsorbed by the cold salt is of course highly probable, but the surface of a fused lump is so small that the weight of this adsorbed air must be negligible. One would here expect a lower result from the salt fused in a vacuum, if gas were dissolved in the other experiments, but the results were, in fact, slightly higher, although not beyond the probable limit of experimental error. It appeared from tests with indicators that the salt remained strictly neutral after fusion in a vacuum, as it did in the air.

Being unable to conceive of any other sensible inaccuracies which could affect the analyses of the chloride of sodium, we turned our attention next to the composition of the chloride of silver, because of the before-mentioned suspicion that Stas was here also in error. An additional reason for this revision is found in the fact that this atomic weight of iodine, found at about the same time, has been found to be about 0.1 per cent too low. (Ladenburg, *Ber.*, xxxv., 2275; Scott, *Proc. Chem. Soc.*, xviii., 112; Köthner and Aeuer, *Ber.*, 1904, xxxvii., 2536, and *Liebig's Ann.*, 1904, cccxxxvii., 123, 362; Baxter, *Proc. Amer. Acad.*, 1904, xl., 419).

THE SYNTHESIS OF ARGENTIC CHLORIDE.

Many accurate analyses were made by Stas which involve more or less directly the atomic weight of chlorine,

but of these we are concerned in the present paper only with those which compare silver with chlorine, because such alone could cause an error leading to the discrepancy under discussion. The experimental solution of the problem is thus a comparatively simple matter, to be accomplished by combining silver with chlorine. Among all Stas's experiments there seems to have been only seven which dealt directly with this ratio ("Untersuchungen," trans. Aronstein, 1867, 173, 175; ex. "Oeuvres," i., 333). These were carried out by two methods. Of these methods, one, the ignition of silver in a stream of chlorine, is acknowledged by Stas to possess errors which he could not wholly correct. Hence the three experiments made by this method are of doubtful value, and only four analyses remain for the purpose of obtaining directly this very important ratio. Even in these the large glass globes employed were more or less attacked by the strong acids or the fused chloride, and, moreover, Stas questioned the purity of the silver used in one case (Aronstein, p. 117; "Oeuvres," i., 330). There is obviously no doubt of the need of obtaining more light upon this matter.

The fundamental requirements of a satisfactory synthesis of argentic chloride are as follows:—First, that the silver must be pure; secondly, that it must all be collected in the argentic chloride, and thirdly, that this argentic chloride must be pure. Because all the error accumulates upon the consequent atomic weight of chlorine and is magnified in calculation, the requirements are usually rigorous.

The fulfilling of the first of these requirements has already been treated in detail, under the discussion of the preparation of silver. Our knowledge of the essentials of this easy but subtle process grew as the quantitative work on the synthesis of the chloride progressed. Whether in the future anyone may be able to discover an unsuspected source of impurity in our purest silver, is of course impossible to say. At least there can be no doubt that it was of distinctly a higher grade than the silver used by Stas in most of his work.

In order to convert this silver wholly into the chloride without loss or illegitimate gain, two methods were used, for fear that in one of these a constant error might lurk unsuspected. The first consisted in the usual method of solution in nitric acid and precipitation in dilute solutions, being essentially similar to that used in obtaining the ratio between common salt and silver chloride. The weighed silver was dissolved with all the precautions used in previous work and precipitated as chloride by hydrochloric acid at concentrations of about fifth normal. Hydrochloric acid was added in excess and the precipitate was washed three times with dilute hydrochloric acid, in order to diminish as much as possible the solubility of the silver salt. After collection on a Gooch crucible, drying at 150°, and washing the bulk of the precipitate was fused in a porcelain or quartz crucible and the loss in weight by fusion determined.

It would appear at first as if the result of this process could furnish nothing not directly calculable from a comparison of the two sodium series, in one of which common salt was compared with silver and in the other with argentic chloride. This is not true, however, for in this previous work the precipitate formed in the presence of sodic nitrate and excess of argentic nitrate, while in the present case an occluded alkaline salt could not be carried down, because none was present, and *all* the silver could be converted into chloride. For this reason the synthesis of argentic chloride in the presence of nothing but volatile substances is an important step in the work.

As usual, in this case also, improvement was effected as the work progressed, and here as before the less perfect tentative work is included in the table (Preliminary Series). The synthesis of argentic chloride is a process of greater certainty than a metathetical reaction, for the reasons just stated, and hence, finer corrections could be discovered and applied.

These corrections, in addition to the two already

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SYNTHESIS OF ARGENTIC CHLORIDE.

Preliminary Series.

No. of expt.	Description of silver. Sample, support, and environment during fusion.	Observed weight of silver (vac.).	First approximate weight AgCl (vac.).	Corrections to AgCl.				Corrected weight AgCl (vac.).	Parts of AgCl produced from 100'000 parts Ag.
				Asbestos residue (add.).	Loss on fusion (subtr.).	Gain in Cl ₂ (add.).	Cor. for solubility (add.).		
65.	P, lime, vac. . .	Grms. 9'06483	Grms. 12'04416	M.grm. 0'10	M.grm. 0'79	M.grm. 0'12	M.grm. 0'06	Grms. 12'04365	Per cent. 132'861
66.		8'39217	11'14987	0'35	0'57	0'14	0'06	11'14985	132'860
70.		5'37429	7'14072	0'26	0'51	0'03	0'06	7'14056	132'865
Average 132'862									
67.	P, carbon, blast	8'08222	10'73844	0'46	0'49	0'22	0'06	10'73869	132'868
68.		7'08517	9'41382	0'20	0'50	0'04	0'06	9'41362	132'864
71.		7'97715	10'59854	0'45	0'82	0'14	0'06	10'59837	132'859
Average 132'864									
72.	S, lime, vac. . .	8'11978	10'78751	0'36	0'38	0'09	0'09	10'78767	132'857
73.		8'53452	11'33904	0'28	0'40	0'09	0'06	11'33907	132'861
74.		6'73284	8'94497	0'42	0'51	0'14	0'09	8'94511	132'858
75.		8'91366	11'84225	0'48	0'48	0'09	0'06	11'84240	132'857
76.		9'72295	12'91736	0'56	0'41	0'09	0'09	12'91769	132'858
Average 132'858									
79.	U, carbon, H ₂ .	8'63961	11'47877	0'30	0'61	0'07	0'09	11'47862	132'860
R. 1.	V, lime, blast..	11'13795	14'79856	0'24	0'50	0'10	0'09	14'79849	132'865
Total average 132'861									
Stas found 132'848									

Final Series.

69.		7.24427	9.62517	0.16	0.40	0.09	0.06	9.62508	132.865
77.		8.30502	11.03312	1.10	0.14	0.67	0.09	11.03484	132.870
78.		7.29058	9.68547	1.23	0.12	0.09	0.09	9.68676	132.867
80.		8.58472	11.40578	0.57	0.32	0.02	0.09	11.40614	132.866
81.		8.01318	10.64632	0.34	0.32	0.05	0.09	10.64648	132.862
R. 2.		9.77160	12.98283	0.74	0.37	0.02	0.13	12.98335	132.868
83.		7.98170	10.60528	—	—	—	—	10.60528	132.870
Average									132.867
R. 3.		11.49983	15.27978	0.44	0.66	0.03	0.05	15.27964	132.868
84.		6.25318	8.30834	—	—	—	—	8.30834	132.866
85.		7.72479	10.26360	—	—	—	—	10.26360	132.866
Average									132.867
Total (Final Series) ..		82.66887						109.83951	132.867

heeded, namely, that for the asbestos shreds carried away during filtration and that for the inclosed wash water set free on fusion of the chloride, were five in number.

The first of these was a correction for the presence of a trace of argentic chloride clinging to the collected asbestos shreds. This silver salt lost chlorine on ignition—a quantity which was determined by dissolving the residual silver and titrating with N/100 sulphocyanate. The amount of chlorine thus lost on the average was 0.02 m.grm. in each synthesis—an amount which was added to the weight of the asbestos shreds. This correction might in most cases have been omitted, but it was determined for the sake of certainty.

The second of these corrections was for the slight solubility of argentic chloride even in dilute hydrochloric acid. This solubility may have been only apparent, the trace found being due to the imperfection of even the double filtration through asbestos and filter-paper—but in any case it needed determination and correction. The average solubility, from five determinations (p. 203), was one part in 30,000,000 of water, which is about the order of the possible solubility of *undissociated* argentic chloride, and

hence may have represented that quantity. The determination was made by evaporating the hydrochloric acid solutions, rinsing out the dish with ammonia, and testing the resulting solution nephelometrically by comparison with similarly prepared known solutions of silver chloride, as has been said.

The third correction was for an occasional loss of chlorine by the argentic chloride on fusion, owing either to the presence of argentic nitrate or to traces of dust. The darkening thus caused represents a real, although often trivial, deficiency of weight; but, fortunately, this is easily restored by fusion in a mixture of pure chlorine and hydrochloric gas. Of course this process must not be adopted when argentic nitrate is included during the analysis of a metallic chloride, for it would then lead to a large excess of argentic chloride; but it is perfectly safe in the present case. The only suspicion which attaches to it is the possibility that an *excess* of one of these gases might be dissolved. This is undoubtedly a real danger, unless the fused salt is exposed to the air and agitated in contact with it while fused. If this is done, we have assured our selves by repeated experiments, that no essential excess of

chlorine remains dissolved. (Dr. Baxter, *Proc. Amer. Acad.*, 1904, xl., 432, has come to the same conclusion; and so also have Köthner and Auer, *Liebig's Annalen*, 1904, cccxxxvii., 127). Two facts pointed to this conclusion:—First, that those samples of argentic chloride, which after the preliminary fusion merely in air were perfectly colourless, transparent, and pearly, gained no essential weight on fusion in chlorine (Expts. 80, R. 2, and R. 3, Final Series); and, secondly, that argentic chloride fused in chlorine, properly freed from it, and subsequently again and again fused in pure air, lost no essential weight.

We always secured elimination of the possible trace of dissolved chlorine by continuing to fuse in air with occasional removal of the cover, and by carefully rolling the inclined crucible around, while held with forceps, during the solidification of the fused mass. Spreading the solid in this way makes it easier to fuse the salt once more without breaking the very fragile quartz crucibles.

The attacking of glass by chlorine in contact with silver chloride, and a consequent loss of weight, gave Stas considerable difficulty. Baxter has found that even porcelain is attacked in displacing iodine with chlorine in the silver salts. We did not greatly fear a loss of weight of the porcelain crucibles, since our chlorine was dilute, and was applied only for a few minutes; nevertheless, we adopted the use of quartz as an added precaution in the later experiments. No difference in results could be detected by its use.

A fourth correction which we sought to determine was for the possible volatility of the argentic chloride during fusion. The constancy of weight on repeated fusion, already mentioned, seems to be sufficient proof for considering this correction as negligible. The conclusion is strengthened by the results of Biltz and Victor Meyer, who found argentic chloride to be but slightly volatile at much higher temperature (*Ber.*, 1889, xxii., 727). It is not, of course, contended that argentic chloride has no vapour-tension at 500°, but only that the loss occasioned by its evaporation is too small to receive consideration.

(Köthner and Auer, *Liebig's Annalen*, 1904, cccxxxvii., 128, found a volatilisation of only 0.0002 in a case where several litres of gas had been passed over argentic chloride during several hours. This agrees essentially with our result, for the likelihood of distillation in our case was much less).

During fusion, however, there is sometimes a slight spurting or projection upward of minute drops of fused material. Hence the crucible must always be covered with an accurately weighed lid—a precaution which was always taken in the final experiments.

The phenomenon of spurting suggested that weighable quantities of air may be absorbed during fusion in air, and led to our effort to discover a fifth correction. Carefully conducted experiments showed, however, that there was no loss in weight of 3 grms. of ordinarily fused argentic chloride when fused again in a vacuum. The fusions were conducted in a porcelain boat covered with another inverted to serve as a lid. Slight traces of enclosed gas were noticed by Stas in many substances, but our quantitative experiments showed that they do not amount to a weighable quantity either in common salt or silver chloride. Thus, all the final experiments in this paper refer to substances fused *in vacuo*, and hence presumably as free as possible from enclosed air.

There were thus seven possible corrections, besides the correction of the weights to the vacuum standard, which might be applied to the results. Two of these, that for the possible volatility of argentic chloride and that for weight of dissolved air, were so small as to be entirely negligible. The chlorine lost from the traces of argentic chloride clinging to the displaced asbestos shreds was added to the weight of these shreds, and is included therein in the table. The three other corrections are recorded in detail in the table, which contains the original weight of the precipitate dried at 150°, as well as the final corrected values. The almost negligible correction for the solubility

of argentic chloride in dilute hydrochloric acid was computed, in the Preliminary Series, from the volume of the washings.

A few inessential changes in the mode of precipitation were occasionally introduced. In Experiments 75, 76, and 79 both solutions were only about tenth normal, and the number of washings was diminished; in R. 1 the argentic nitrate was very dilute, but the hydrochloric acid was somewhat concentrated.

As has been said, the tentative experiments were all classed together in the Preliminary Series. The table explains itself, for the most part, except perhaps the second column. This defines in the first place the designation of the silver, next the nature of the containing vessel on which it was fused, and last the atmosphere surrounding the metal during fusion. The word "blast" signifies that the sample thus qualified was fused in a blast-flame of illuminating gas and air, delivered from a clean nozzle, and that the resulting mass was cooled in the reducing flame.

Although not giving the true amount of chloride to be obtained from the purest silver, this table was highly instructive. It showed in the first place that even silver of this grade of purity must be 0.01 per cent purer than that of Stas.

(There can be no doubt that this difference is due to the fact that Stas fused all the silver used in this part of his work in a porcelain crucible under borax and nitre, thereby introducing both alkali and oxygen ("Oeuvres," i., 328). His own subsequent experiments (*Oeuvres*, i., 466) showed that this metal was at least 0.005 per cent less pure than his distilled granulated silver, which must, in its turn, have contained some oxygen. His still later elaborate search for oxygen in the silver is not satisfactory, because just before determining the oxygen in it he ignited it in a reducing flame, and because he sought to determine the oxygen only by heating to redness in a vacuum, a process which may have set free only the superficial oxygen. Dumas (*Ann. d. Chim. Phys.*, 1878, xiv., 289) found 0.008 per cent of oxygen in similar silver by fusion *in vacuo*, and Mallet (*Phil. Trans.*, 1880, clxxi., 1020) found that silver fused like Stas's purest in the oxyhydrogen blast contained 0.005 per cent of oxygen).

Again, it showed that at least a part of the difference between the two new values for the atomic weight of sodium is due to an error in the assumed atomic weight of chlorine used in the calculations. It proved that the analytical method was capable of yielding very constant results with a given sample of silver (Exps. 72–76). It confirmed previous results in showing that portions fused in these various ways were not very different, but showed slight variations according to the method of fusion employed (see Richards, *Proc. Am. Acad.*, 1893, xxix., 65). It furnished a means of determining, by later comparison of one or the other of these results with those from the purest silver, the exact grade of purity of the various specimens of silver used in the previous work in this laboratory, in particular that used in the earlier part of the present research. Finally, it furnished sufficient clue to the precautions which must be taken to secure yet purer silver.

A careful study of the accompanying table led to the conclusion that a reducing environment is necessary to eliminate traces of oxygen during fusion, and that lime is better than carbon as a support during fusion. The details of this matter have already been described (p. 194) under the heading "Preparation of Pure Materials," and need not be further detailed here. Suffice it to say that the silver used in the experiments recorded in the table (Final Series) was free from the sources of error thus detected.

The Final Series comprehends ten experiments, made with four samples of silver prepared entirely independently by three different experimenters (Dr. Baxter having very kindly given us a piece of his purest silver used in the determination of the atomic weight of iodine, and each of the authors having made separate samples), and two entirely different methods of synthesis.

Of these methods of synthesis one has already been described, namely, the usual method of solution of the silver in nitric acid, precipitation by hydrochloric acid, and filtration on a Gooch perforated crucible. Of course all the precautions and corrections already discussed were applied with as much care as possible. All the vessels used were afterwards washed with a little ammonia, and the washings tested nephelometrically in order to be sure that no silver was lost by adsorption on the vessels. By this method Experiments 69, 77, 78, 80, 81, R. 2, and R. 3 were made. Further unvaried repetition of this process seemed to promise no further light on the question.

Although this method seemed to leave little or nothing to be desired as regards accuracy, it was nevertheless deemed advisable to test it by making a few syntheses by means of entirely a different process, in which all the vessels coming in contact with the precipitate could be weighed. Accordingly, a new method was devised, a modification of one of those used by Stas, employing quartz vessels instead of glass. A quartz dish was accurately weighed by substitution of a counterpoise of a similar composition, surface area, and weight. A watch-glass to serve as its cover was weighed in a similar fashion separately. A weighed piece of silver was placed in the dish, which was supported in a large empty "desiccator," whose bottom and sides were well moistened with pure water. The silver was covered with re-distilled nitric acid of the usual strength, and left covered both by watch-glass and desiccator lid to dissolve slowly over-night in a warm place. On the next day the moisture on the glass cover was washed, with great care to avoid the slightest spattering, into the quartz dish. If any spattering occurred it was caught in the large desiccator, which, having been tightly covered, served also to catch all spray proceeding from the solution of the silver. In two experiments, the silver recovered from the water in the desiccator amounted to only 0.02 m.grm. when estimated by the nephelometer, and in one no silver at all was found in the desiccator.

Hydrochloric acid gas was next allowed to play upon the surface of the silver nitrate solution in the quartz dish, and the resulting chloride was caused to sink to the bottom by means of a very small glass stirrer, afterwards carefully rinsed. The remaining solution of nitric and hydrochloric acids was then evaporated to dryness upon a clean steam-bath under an appropriate hooded cover (Victor Meyer funnel). The atmosphere around was kept as pure as possible during this evaporation, which was usually conducted during the night. Finally, the silver chloride was fused in the quartz dish supported inside of a large porcelain crucible from which the products of combustion of the gas-flame were suitably deflected. The weighed cover caught the one or two minute drops projected upward during the act of fusion. Then a mixture of chlorine and hydrochloric acid gas was passed in, so as to convert any residual traces of nitrate of silver wholly into argentic chloride. The precaution of cooling mentioned above enabled us to preserve the quartz dish intact through the analyses, notwithstanding the extreme fragility of thin fused quartz. Its weight was conserved through three experiments within the limits of the accuracy of the weighing. Experiments 83, 84, and 85 were made by this method. One of these is given below in detail as an example of the method.

Experiment 84.

	Grms.
Corrected weight of silver in air	6.25336
Vacuum correction	0.00018
Weight of silver in vacuum	6.25318
Excess weight quartz dish over counterpoise ..	0.21510
Excess weight dish and fused AgCl over counterpoise	8.52279
Weight of argentic chloride in air	3.30769

Excess weight cover glass over counterpoise ..	0.00972
Excess weight cover and spattering over counterpoise	0.00974
Spattering	0.00002
Weight argentic chloride in air	8.30771
Vacuum correction	0.00061
Weight of argentic chloride in vacuum	8.30832
AgCl found in desiccator by nephelometer	0.00002
Total weight of argentic chloride	8.30834
AgCl = $6.25318 : 8.30834 = 100.000 : 132.866$.	

This second method, which avoids any transference of material whatever, is an unusually searching check upon the method employing the Gooch filter, and that the two methods confirm each other to the limit of weighing is a most satisfactory criterion of each, supporting the previous similar work with sodic chloride as well.

The Final Series is complete, including all the experiments made with the purest material, and every precaution. The experimental work, as well as the preparation work, was the product of more than one experimenter, the senior author having made, from beginning to end, the syntheses numbered R. 2 and R. 3 (as well as R. 1 in the Preliminary Series), and the junior author having made all the others. The two experimenters used different balances, different weights separately standardised, and different preparations throughout, in order to secure additional certainty.

(The hydrochloric acid used in Experiments R. 1, R. 2, and R. 3 was three times successively treated with small amounts of permanganate, and boiled to eliminate bromide, and each time distilled).

For No. 69, Baxter's silver fused on lime in hydrogen was used; for Nos. 77, 78, 80, 81, 83, R. 2, sample T, fused in the same way; for R. 3, sample V, fused on lime in a vacuum, and for 84 and 85 sample W, fused on lime first in hydrogen and then in a vacuum.

The result, namely, 132.867 parts of the chloride from 100,000 of silver, has a "probable error," computed according to the method of least squares of about 0.0005. This so-called probable error of course gives no clue as to possible constant errors involved. A better idea of the chemical trustworthiness of the result is got by comparing the data furnished by the two different methods of synthesis. The averages of the seven determinations by the method of filtration is 132.8666, while that of the three by the method which involves no transference of material (83, 84, 85) is 132.8673. These are both within the range from the mean 132.8668 indicated by the "probable errors" of the respective averages, and hence may be considered as identical.

If the comparison be made according to the environment of the silver during fusion, a similar result is obtained. The silver fused in hydrogen gives an average of 132.8668, while that fused in a vacuum gives 132.8668. Again this is essential identity.

In view of these facts, the fact that all probable errors tend to lower the result, and the multitude of precautions which eliminated error from these figures, it is not unsafe to conclude that 100,000 parts of the purest silver really yields as much as 132.867 parts of argentic chloride. This conclusion confirms the comparison of the silver and argentic chloride indicated by the work on sodium, and shows that no great occlusion of sodic nitrate could have taken place there. It furnishes, moreover, a means of determining by comparison the purity of any other specimen which has been used in the quantitative synthesis of argentic chloride by either of the foregoing methods. For example, it shows that the silver used in the work on sodium—silver which yielded 132.862 parts of chloride—must have contained $\frac{132.862}{132.867} = 99.977 = 0.0037$ per cent of impurity.

(See Syntheses 65, 66, and 70 given in the table. The silver used in these syntheses was exactly similar to some of that used in the work on sodium. In the same way, if Stas's method of synthesis is considered as comparable with ours, his silver must have contained $(132867 - 132848) \div 132867 = 0.015$ per cent of impurity. If is doubtful, however, if the methods of synthesis are strictly comparable).

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 20, May 14, 1906.

Conductivity of Ammonium Sulphate in Mixtures of Sulphuric Acid and Water.—G. Boizard.—When ammonium sulphate is dissolved in mixtures of varying proportions of sulphuric acid, and water, solutions are obtained whose conductivity is greater or less than that of the solvent. As a result of his experiments on this subject, the author asserts that the phenomenon shown by ammonium sulphate is general. This he proves by dissolving in mixtures of sulphuric acid and water—(1) All the sulphates, whether anhydrous or hydrated; (2) the bisulphates; (3) the mineral acids and a number of organic acids; (4) such salts as MnO_4K , $\text{PO}_4\text{H}(\text{NH}_4)_2$, NaCl , NO_3K , $\text{CH}_3\text{CO}_2\text{Na}$, &c.

Total Synthesis of Camphor Derivatives. Isolaurene and Isolaurenic Acid.—G. Blanc.—The author completes the synthesis of the camphor derivatives, and states that this has only become practicable since the execution of the total synthesis of the $\alpha\alpha$ -derivatives of dimethyladipic acid, and also by certain improvements in the methods which he devises.

α -Chlorocyclohexanone and its Derivatives.—L. Bouveault and F. Chereau.—When chlorine acts on cyclohexanone, an α -chloro-derivative is obtained, but the hydrochloric acid which is formed at the same time causes the production of certain condensation products. The best results are obtained by performing the chloruration in presence of calcium carbonate in water. The results are still better if cyclohexanol is used instead of cyclohexanone, but a double quantity of chlorine must be employed. The α -substituted homologues of cyclohexanone can thus be prepared without difficulty, e.g., α -methylcyclohexanone, which boils at 160° under 10 m.m. pressure, its semicarbazone melting at 195° . α -Ethylcyclohexanone boils at 65° under 10 m.m. pressure, and its semicarbazone melts at 157° ; also α -isopropylcyclohexanone, boiling at 80° under 10 m.m. pressure.

Stereoisomerism in the Group of the $\alpha\beta$ -Acyclic Non-saturated Acids.—E. E. Blaise and P. Bagard.—The investigation and isolation of the non-saturated stereoisomeric acids has hitherto presented great difficulties—the majority of chemical, and even physical, agents transforming the labile isomers into the stable isomers. The authors now succeed in overcoming this difficulty and utilising M. Bodroux's reaction. They find that the ethers of the labile acids give the corresponding amides without transposition when they are treated with the bromomagnesium derivatives of the amines. These amides, which easily crystallise and can be separated, can be used for a precise investigation and a certain identification.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 7, 1906.

Two Acid Sodium Sulphates.—J. D'Ans.—Trisodium hydrosulphate, $\text{Na}_3\text{H}(\text{SO}_4)_2$, may be prepared by evaporating a solution containing equimolecular quantities

of sodium sulphate and sulphuric acid, when crystalline needles separate out on cooling. When a solution containing 16.5 per cent of sulphuric acid and 35 per cent of sodium sulphate is warmed, and sodium sulphate and sulphuric acid are added gradually, in the proportion of 10 grms. of the salt to about 2 c.c. of concentrated acid, crystals of $\text{Na}_3\text{H}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ separate out. Their formation is accelerated by the addition of a crystal to the solution.

Dissociation of Barium Carbonate.—Alexis Finkelstein.—The study of the dissociation of barium carbonate has been found very difficult, because high temperatures have to be employed, and baryta when hot attacks the material of which the vessels containing it are made, such as platinum, porcelain, and all silicates; the author, however, has found that the exclusion of oxygen stops the action, and that in pure nitrogen baryta and platinum do not act on one another. From the curves he obtained it appears that the dissociation of barium carbonate occurs in two phases; first a basic carbonate is formed; this is easily fusible, melting below 950° . Its composition appears to be $\text{BaCO}_3 \cdot \text{BaO}$, and it is capable of dissolving BaO and also BaCO_3 at a higher temperature. This compound then decomposes into BaO and CO_2 . Barium carbonate melts at a temperature above 1350° . The heat of the dissociation reaction does not vary with the temperature.

Elementary Analysis with the Dennstedt and Heräus Furnaces.—D. Holde.—The author has investigated the question of the advantages to be gained by the use of electric instead of gas furnaces for elementary analysis. Using a Heräus furnace he finds the cost considerably greater than with a glass furnace, but the electric apparatus requires no special combustion room as the surroundings are not heated. The operation is as trustworthy as with gas and takes the same time, but need not be watched so long, while one great advantage is that the temperature of the air round the furnace is not raised, so that the experimenter suffers no inconvenience. With the Dennstedt furnace the combustion can usually be accurately performed in from fifteen to twenty-five minutes, except in the case of certain substances, but the disadvantage of the furnace is that during the quick analyses it must be watched incessantly.

Action of Light on Uranyl Acetate.—A. Bach.—When carbon dioxide is led through a solution of uranyl acetate exposed to direct sunlight the salt is reduced to a mixture of uranous and uranic hydrates. The salt suffers no such change if it is exposed to light in the absence of carbon dioxide, or if carbon dioxide is introduced in the dark. This result has been disputed by Euler, but the author has repeated the experiments and confirmed his conclusions. He finds that if the illumination, concentration of uranyl acetate, and diameter of the tube in which the salt solution is placed are kept constant, the time taken for the appearance of a definite turbidity is inversely proportional to the height of the liquid, and when the ratio between this height and the diameter has reached a certain value the reduction ceases. When illumination, diameter, and height of column of liquid are constant, the time of reaction varies inversely as the concentration of the solution. Hot saturated solutions are almost instantaneously reduced.

New Method of Preparing Ketones.—Hugo Haehn.—Commercial calcium carbide reacts in the cold with any fatty monocarboxylic acids, yielding acetylene. When this reaction takes place at a higher temperature the ketones may be directly obtained, two molecules of acid giving off water and carbon dioxide, $\text{R.COOH} = \text{R.CO.R} + \text{CO}_2 + \text{H}_2\text{O}$. The water acts on the carbide, yielding acetylene and calcium oxide, or the hydrate is left behind. A combustion tube is filled with pieces of calcium carbide as large as a pea; the acid is allowed to drop slowly into one end of the tube, which is heated in a combustion furnace, and the ketone is collected

in a receiver at the other. The raw ketone should be neutral. If it has an acid reaction either the distillation is proceeding too quickly or the temperature of the carbide is not high enough.

MISCELLANEOUS.

The Electrician.—Mr. W. R. Cooper, M.A., B.Sc., M.I.E.E., A.M.Inst.C.E., has been offered and has accepted the position of Editor of *The Electrician* in the place of Mr. F. C. Raphael, A.M.I.E.E., who retires on June 30th.

Literary Note.—Messrs. Archibald Constable and Co. will shortly publish "Chemistry of Paints and Paint Vehicles," by C. H. Hall. The book is written from the standpoint of a Chemist actively employed in the manufacture of Paints and Colours, and it is a practical book for practical men.

MEETINGS FOR THE WEEK.

WEDNESDAY, 20th.—Microscopical, 8. "On the Structure of some Carboniferous Ferns," by the President.

THURSDAY, 21st.—Chemical, 8.30. "Cleve Memorial Lecture," by Prof. T. E. Thorpe. "Constituents of the Essential Oil from the Fruit of *Pittosporum Undulatum*," by F. B. Power and F. Tutin. "Mobility of Substituents in Derivatives of β -Naphthol," by J. T. Hewitt and H. V. Mitchell.

FRIDAY, 22nd.—Physical, 5. "Effect of Radium in Facilitating the Visible Electric Discharge *in vacuo*," by A. A. Campbell Swinton. "Comparison between the Peltier Effect and other Reversible Heat Effects," by A. O. Allen. "Effect of the Electric Spark on the Activity of Metals," by T. A. Vaughton. "Dielectric Strength of Thin Liquid Films," by P. E. Shaw. "Effect of Electrical Oscillations on Iron in a Magnetic Field," by W. H. Eccles.

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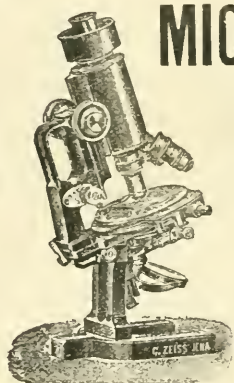
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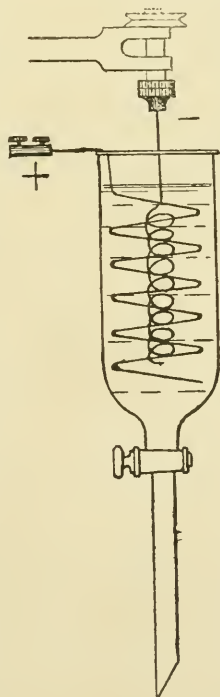
A SIMPLE FORM OF ROTATING ELECTRODE FOR ELECTRO-CHEMICAL ANALYSIS.*

By F. MOLLWO PERKIN, Ph.D.

AT the first meeting of the Faraday Society I published a note upon a rotating electrode for electro-chemical analysis (*Electrochemist*, iii., 26). It consisted of a sand-blasted gauze cylinder fastened on to the end of a stout iridium-platinum wire, and which was rotated within a circular anode. The anode was made of two rings of thick platinum wire which were connected together by four small baffles. The object of the baffles was to prevent the liquid being swirled round in the electrolysing vessel by the rapid rotation of the cathode. The results obtained with this electrode were quite satisfactory, and in their paper on the "Electrolytic Deposition of Zinc," Dr. Price and Mr. Judge have also obtained very satisfactory results with this form of cathode.

As it is always an advantage to use the simplest possible apparatus for analytical purposes, more especially apparatus which can readily be obtained or at any rate constructed in any laboratory, it occurred to me to endeavour to simplify the cathode for rotation work. The cathode as originally described could not be made in the laboratory, but the one which I have recently adopted can be made without any difficulty.

As will be seen from the diagram the cathode simply consists of a spiral of platinum wire. It is, however, best to use iridium-platinum wire because this is much more rigid and the electrode is less likely to "throw out" when rotated at high speeds. The electrode originally employed was made of ordinary platinum wire, 1 m.m. in diameter. The ones at present in use are made from an alloy of platinum with 20 per cent of iridium. It must be admitted that as this alloy is very hard it is not easy to coil into a spiral, and it is therefore better to get the makers (Messrs. Johnson, Matthey, and Co.) to make the spiral when ordering the wire. It is a further advantage to have the spiral sand-blasted; for a great many metals, however, this is unnecessary. The total active surface of the electrodes now in use is about 23 sq. c.m. The anode consists of a 1 m.m. platinum wire wound into two or three spirals so as to fit tightly against the electrolysing vessel. It will be noticed that I use the same apparatus, viz., a tap funnel, for holding the solution to be analysed as that described by Dr. Price and Mr. Judge, and I am indebted to them for the suggestion. This form of electrolysing cell is extremely useful and very simple, and is of great advantage for washing the deposited metal without stopping the current or removing it from position.



Below is appended the results obtained with this form of cathode in the analysis of copper.

CuSO ₄ taken.	Current in amperes.	E.M.F.	Time in minutes.	Deposited copper.
0.0506	0.45—4.8	2.7—6.0	35	0.0498
0.1013	0.6—2.0	2.8—4.8	38	0.1005
0.1266	1.0—5.5	3.0—9.0	32	0.1253
0.1013(a)	0.5—2.0	5.0—7.6	40	0.1009
0.1266	0.45—3.0	—	40	0.1266
0.1266	0.5—4.5	—	35	0.1263

(a) From cyanide solution.

The bulk of solution was in all cases about 50 c.c., and the quantity of concentrated nitric acid added from 0.5 to 1 c.c.

Owing to the extremely high cost of platinum, one would often like to employ less expensive metals for cathodes. I might say that a spiral of nickel wire can quite satisfactorily be employed for a good many metals; for example, for copper, zinc, or iron. The metals are readily removed by means of, in the case of copper, moderately strong nitric acid, and it is surprising how little the nickel itself is acted upon by this acid. In the case of zinc or iron dilute hydrochloric or sulphuric acid may be used, and also against these acids the nickel is very fairly resistant. Of course, when nickel electrodes are used it is necessary to weigh them after each determination before they are again used. With platinum this is not absolutely essential, but it is always a wise precaution to take. I have an electrode of nickel wire which has been used fifteen times for copper and nickel determinations, and it looks as if it might be used for quite another forty such determinations.

Platinum is usually regarded as a metal which is practically unacted upon by reagents, with the exception of aqua regia. When employed in electro-chemical work as an anode, however, it is by no means so stable as it is generally considered; this is especially the case when high current densities are employed. For example, in potassium cyanide solution the platinum is distinctly soluble, as the following numbers will show. A weighed anode of platinum wire having a surface of about 10 c.m. was placed in a 4 per cent solution of potassium cyanide, and a current of 4 amperes passed for thirty-five minutes. At the end of the time the platinum had lost 0.0016 gm. It was again placed in the solution, and a current of 3 amperes passed for fifty minutes; the loss in weight was now 0.0015 gm. In this connection it should be of interest to electro-chemists to hear that Messrs. Johnson, Matthey, and Co. are now supplying iridium of over 99 per cent purity. I am informed that this is the first occasion that the metal of such a high state of purity has been obtainable. The metal is as hard as steel, and may be boiled in aqua regia without being attacked; it is also unacted upon by molten lead. I understand that the fact of its not alloying with lead is made use of in its preparation. It has not been found possible to draw it into wire, and it can only be rolled into sheets when hot.

Direct Oxidation of Cæsium, and certain Properties of Cæsium Peroxide.—E. Rengade.—It is known that cæsium burns immediately on contact with air. The author investigates the question as to whether this property is due to the presence of water, and also how the metal behaves with regard to pure dry oxygen. As a result of his experiments, he finds that even perfectly dry oxygen does attack cæsium at ordinary temperatures with great energy, and more slowly as the temperature is reduced. The action of excess of oxygen on cæsium causes the formation of the yellow peroxide, Cs₂O₄, which is easily dissociable, and is decomposed by water at ordinary temperatures, and reduced by carbon dioxide and by hydrogen at temperatures very little above normal.—*Comptes Rendus*, cxlii., No. 21.

* A Paper read before the Faraday Society, June 12, 1906.

RELATIVE STRENGTHS OF ACIDS.

By PHILIP BLACKMAN.

ARRHENIUS showed that if acids be arranged in the order of their relative strengths they were also arranged in the order of their molecular conductivities (W. Ostwald, "Lehrbuch der Allgemeinen Chemie," II., i., 650). The comparison in practically all cases is so remarkably close that the electrical conductivity method has been accepted as a means for determining the relative strengths of acids. A satisfactory explanation (on the hypothesis of the "degrees of dissociation of acids") has been advanced to establish the connection between the relative strengths of acids and their molecular conductivities, and in this paper an attempt is made to supply a proof.

It was shown by the author ("Quantitative Relation between Molecular Conductivities," *Phil. Mag.*, 1906, xi., 416) that $\mu_{v_{HX}} + \mu_{v_{M_1OH}} - \mu_{v_{M_1X}} = K$ (a constant); where $\mu_{v_{HX}}$, $\mu_{v_{M_1OH}}$, and $\mu_{v_{M_1X}}$ represent respectively the molecular conductivities (measured at the same molecular concentration, v , and at the same temperature) of the acid HX , the base M_1OH , and the salt M_1X . This value K represents the loss of electrical conductivity corresponding to the equation $H \cdot + X' + M_1 \cdot + OH' = H \cdot OH + M_1 \cdot + X' + K$ or $H \cdot + OH' = H \cdot OH + K$. It is reasonable to conclude that, had there been in the final solution $H \cdot$ and OH' ions (*i.e.*, $H \cdot + OH' = \text{not } H \cdot OH$, but $H \cdot + OH'$), the value of K would have been equal to zero. In other words, K would represent the molecular conductivity of water—under the conditions mentioned, *viz.*, (1) temperature and (2) molecular concentration.

It was shown that K is a constant for each series only, but is not a common constant for all series, *i.e.*, K varies with the nature of the acid. This can be explained in one of two ways, *viz.*, either (1) the "molecular conductivity" of water is a variable quantity, or (2) the "molecular conductivity" of water is really a constant, the variability being due to the fact that the stronger the acid is the greater does the value of K become, the maximum relative value (at any one temperature and concentration) being reached in the case of the strongest acid. Of these two assumptions, the first is improbable and the second is apparently correct.

Assuming, then, that the molecular conductivity of water is constant, and also assuming for the moment that all acids were of equal strength, it would be a necessary condition that—

$$\begin{aligned} \mu_{v_{HX}} + \mu_{v_{M_1OH}} - \mu_{v_{M_1X}} &= K(HX) \\ = \mu_{v_{HX_1}} + \mu_{v_{M_1OH}} - \mu_{v_{M_1X_1}} &= K(HX_1) \\ = \mu_{v_{HX_2}} + \mu_{v_{M_1OH}} - \mu_{v_{M_1X_2}} &= K(HX_2) \\ = \dots\dots\dots &= \dots\dots\dots \\ = \text{constant} \end{aligned}$$

(supposing that the terms be arranged so that $\mu_{v_{HX}} > \mu_{v_{HX_1}} > \mu_{v_{HX_2}} > \dots\dots$). In practice, however, this constancy is not observed, as acids are not all of equal strength. The equations may, nevertheless be rendered mathematically equal in several ways, the most useful of which is that which will yield quantitative comparative results. By introducing the factors $x_1, x_2, \dots$ and $y_1, y_2, \dots$ respectively, such that $\mu_{v_{HX}} = x_1 \cdot \mu_{v_{HX_1}} = x_2 \cdot \mu_{v_{HX_2}} = \dots$ and $\mu_{v_{M_1X}} = y_1 \cdot \mu_{v_{M_1X_1}} = y_2 \cdot \mu_{v_{M_1X_2}} = \dots$, the above equations become mathematically true. Bearing in mind that the greater the equalising quantities $x_1, x_2, \dots$ are, the smaller must be the respective strengths of the acids, it is at once evident that the relative strengths of the acids, HX , HX_1 , $HX_2, \dots$ are respectively—

$$\frac{1}{x_1}, \frac{1}{x_2}, \frac{1}{x_3}, \dots;$$

or, expressed as percentages,—

$$100, 100/x_1, 100/x_2, \dots$$

But—

$$x_1 = \mu_{v_{HX}} / \mu_{v_{HX_1}}, \quad x_2 = \mu_{v_{HX}} / \mu_{v_{HX_2}} \dots;$$

consequently, the relative strengths of the acids HX , HX_1 , $HX_2, \dots$, expressed as percentages, are respectively—

$$100, 100 \cdot \mu_{v_{HX_1}} / \mu_{v_{HX}}, 100 \mu_{v_{HX_2}} / \mu_{v_{HX}} \dots$$

East London Technical College, London, E.

INVESTIGATIONS ON THE OCCURRENCE OF CHANGES IN THE TOTAL WEIGHT OF SUBSTANCES UNDERGOING CHEMICAL TRANSPOSITIONS.*

(SECOND COMMUNICATION).

By H. LANDOLT.

(Continued from p. 274).

PROCESS.

THE experiments were performed in practically the same way as the earlier ones. The following information may be given concerning the details of the methods used:—

1. Reaction Vessels.

For most of the experiments η -shaped tubes of Jena apparatus glass were used; their limbs were 10 c.m. long and 5 c.m. across. On the upper bent connecting piece, of length 8 c.m. and diameter 2 c.m., were fixed the two short filling tubes 0.7 c.m. wide. Weight of the full apparatus, 360 to 450 grms.; external volume, 400 to 450 c.c.; external glass surface, 370 to 400 sq. c.m.; substances introduced, inclusive of water, 250 to 350 grms. The η -tubes were smaller than those used in the old experiments, when their weight was 700 to 980 grms. and their volume about 900 c.c.

A second kind of apparatus, denoted hereafter by O, consisted of a glass cylinder (A), 12 c.m. high and 7 c.m. wide, closed at the bottom and ending in a filling tube at the top. In the interior of A, at the bottom, an uncovered glass beaker (B) was fused; its height was 8 c.m. and width 5 c.m. Thus a circular space was formed, in which was placed one of the reacting substances, while the other was put inside the beaker B. Finally, the cylinder was surrounded by another larger closed Dewar's glass enveloping vessel C, 13 c.m. high and 8 c.m. across, the space between A and C being exhausted. Thus the volume of the outer vessel C is unaltered by the changes of volume which the vessel A might undergo in consequence of the heat of the reaction. Weight of apparatus when filled, 450 to 550 grms.; contents, 170 to 260 grms.; external volume, about 600 c.c.; external surface of the glass, about 350 sq. c.m.

Thirdly, I used for some experiments η -shaped vessels of quartz glass, which had been made by Herr Heraeus, of Hanau. They were the same size as the η -tubes of glass, but possessed only one opening for filling, at the highest point of the arch. This was originally closed with a fused mixture of three parts of colophony and one part of wax, and was afterwards closed by fusing in the oxy-hydrogen blowpipe. The vessels have not as yet been much used, because, on account of the great thinness of their walls, there was a fear that an alteration of pressure in the interior would have an effect upon their volume.

Finally, η -tubes of glass were also used, the inner walls of which were covered with a layer of solid paraffin. I was induced to use these because both in the older and more recent experiments I had observed that glass vessels sometimes do not appear to be perfectly impermeable, either in consequence of a little flaw or of an air-bubble in the glass. The presence of such places is noticed in taking the first series of weighings, if the difference of weight of the two vessels undergoes a slight change of the

* From *Sitzungsber. d. K. Akademie d. Wissensch.*, 1906, viii., 266.

same sign from day to day.* The same penetrability, which causes much waste of time, has also been observed by Heydweiller.

All the glass vessels were allowed to lie for several days in dilute sulphuric acid, and then in ammonia, to make their external layer less rich in alkali, and therefore less hygroscopic.

2. Preparation and Adjustment of the Vessels.

When filling the η -tubes with the substances, care was taken to load each limb equally. If this was not possible, as, for example, in experiments on the solution of salts in water, the equalisation was effected by the addition of indifferent substances, such as Bohemian garnets. In most cases, moreover, the liquid surface was covered in one or both limbs of the η -tubes with a layer of paraffin-oil, in order to prevent evaporation.

After fusing up both the reaction vessels, their weight was determined by means of a kilogram. balance which was sensitive to 1 m.grm., and their volume was ascertained by weighing in water at the same temperature. Then for the smaller and lighter vessel a closed addition-body was made of thin glass tubing of diameter 5 m.m., and its volume was altered by immersion in a measuring tube partially filled with water, by means of which 0.02 c.c. could be read off, until the two vessels were adjusted to less than 0.04 c.c. The error caused by the deviations of the weight of the air between the limits 1.15 and 1.25 m.grms. per c.c. thus lay below 0.004 m.grm. The adjustment of the weight to a few m.grms. was performed partly by adding sand to the addition-body and partly by hanging on platinum-wire.

The following is an example of the adjusted apparatus:—

	Vessel A.		Vessel B.	
	Wt. (grm).	Vol. (c.c.).	Wt. (grm).	Vol. (c.c.).
Original vessel .	352.283	393.133	345.019	390.459
Addition body .	—	—	7.566	2.678
Platinum wire .	0.159	0.007	0.155	0.007
	352.744	393.140	352.740	393.153

Difference of weight, 0.004 m.grm.; difference of volume, 0.013 c.c.

For the weighing, the η and O vessels were stored in equally heavy stands of gilded brass, which raised the load on the balance pans to about 490 to 550 grms. In moving the vessels touching with the hand was avoided, an instrument like a fork of polished steel being used. For the purpose of carrying out the reaction, the apparatus was placed on a suitably constructed brass stand, which touched the first only in a few places, and the mixture of the two substances was effected by gradually inclining the whole arrangement.

3. Balance.

The instrument used was made in the workshop of Alb. Rueprecht, of Vienna, who is famous for the construction of precision balances.† It was capable of carrying 600 grms.; length of brass beam 150 m.m.; end planes connected by means of two crossed knife-edges with the scale suspension; platinum weights of 120, 121, 122, 140, 155.5, 160 m.grms., hung on from outside; mirror and telescope reading to a distance of 3 metres; moreover, the loads could be automatically altered and transported on to the pans by poles of equal length, and, finally, the beam and pans released; sensitiveness for 1 m.grm. at a load of 500 grms., originally 400 scale divisions (tenths of a m.m.), after four years' use, gradually reducing to 280; half the time of oscillation, thirty-five seconds. The balance was placed in a room of the former II. Chemical Institute of the University, and was there exposed but little to disturbances from the street, though a good deal to those from the interior of the building, which, however, could be prevented. The room was heated by a gas-

furnace always burning, with an ethyl chloride regulator, which enabled a perfectly constant temperature to be maintained.

The determination of the difference of weight of the two vessels was performed by Gauss' method, given on p. 310 of the first paper, the loads being exchanged twice and the sensitiveness determined four times. Thus, altogether four oscillation points had to be determined, each of them by releasing the beam three to five times. The details of the method will be explained in the complete article. I will here confine myself to some details of the performances of the balance.

(a) When two cylindrical 400 grms. brass weights, differing from one another by about 4 m.grms., were placed in exactly the same position on the pans, and weighed on different days, the exact differences of weight were:—

4.2588, 4.2591, 4.2589, 4.2584, 4.2576 m.grms.; mean, 4.2586; mean error, ± 0.0003 m.grm. (The mean, and not the probable error, is calculated in the following determinations).

Greatest difference in weighing, 0.0015 m.grm.

(b) In another series of weighings of the same weights the deviations were, however, much, greater, e.g.:—

4.273, 4.260, 4.250, 4.242, 4.260 m.grms.; mean, 4.257 ± 0.005 m.grm.

Greatest difference in weighing, 0.031 m.grm.

(c) The determinations of the differences of weight of the glass reaction apparatus gave the following results:—

I. 3.964, 3.972, 3.958, 3.971, 3.966 m.grms.; mean, 3.966 ± 0.004 m.grm.

Greatest difference in weighing, 0.014 m.grm.

II. 5.816, 5.804, 5.793, 5.839, 5.827 m.grm.; mean, 5.816 ± 0.008 m.grm.

Greatest difference in weighing, 0.046 m.grm.

4. Errors in Weighing.

These were chiefly the results of the following influences:—

(a) *Different Temperature of the Two Beam Arms.*—To ascertain this more exactly, through the copper covering plate of the balance two thermometers were introduced, the large mercury vessels of which were directed towards the middle of each half of the beam and were some m.m. away from it. The projecting scales were read by means of a telescope, being temporarily illuminated from behind for this purpose by means of an incandescent lamp. The thermometers, with which 1/100° could safely be estimated, agreed very well, and during a weighing no difference could ever be observed between them. Nevertheless, there were possibly differences of thousandths of a degree, and as calculation shows, if the length of the beam arm is 150 m.m., the load 500 grms., and the coefficient of expansion of brass 0.000019, a difference of temperature of 0.001° would alter the result of the weighing by about 0.01 m.grm. To ensure uniform distribution of heat, in the interior of the balance on the back wall a thick copper plate was placed, and the case was surrounded by screens as well.

(b) *Uniform Alteration of Temperature of the Two Beam Arms.*—If the load was weighed on different days at varying temperatures it always appeared that increase of heat produced a considerable displacement of all the oscillation points towards the right, and this amounted to about 10 whole, equivalent to a reading of 100 scale divisions for 1°. The left half of the beam must thus expand more than the right. Many determinations of weight, performed at different temperatures, which, however, remained constant during the weighing, gave concordant results. As, however, the whole process of weighing took from one hour to an hour and a-half, sometimes it was unavoidable that the two thermometers uniformly rose or fell some hundredths of a degree. In this case, when Gauss' method was used, the heat effect was compensated, yet the small changes of temperature caused an incipient disturbance of the balance, in consequence of

* Examples of such steady changes are given in the first paper, p. 314.

† It is shown in the price list of this firm for 1902, p. 29, No. 48.

which on repeated releasings greater differences appeared in the equilibrium positions.

(c) *Dissimilar Positions of the Loads on the Scale Pans.*—If the load is not distributed perfectly uniformly round the centre of gravity line from the end knife-edge of the beam, on releasing the balance a shifting of the scale pan with its suspension will take place; this causes an inclination of the planes towards the knife-edges, which are not absolutely sharp, and thus a slight change is produced in the length of the beam. If this amounts to only 0.0001 m.m., and the length of the beam is 150 m.m., and the load 500 grms., the effect upon the result of the weighing will be 0.333 m.grm. In Rueprecht's balance this error is for the most part obviated by the insertion of two crossed knife-edges between the plane suspension and the scale bow; nevertheless, it is necessary to place the load, i.e., the reaction vessel with its stand, as centrally as possible. A special instrument was used for this purpose. It consisted of a balance pan capable of turning vertically, and having on its lower side a point 10 c.m. long, which played against a second point on the pedestal of the arrangement. After the apparatus had been placed by means of guiding pins always in the same central position on the scale pan either by moving the glass vessel on its stand, or, after the reaction had taken place, by pouring the liquid from one limb of the Π -tube into the other, the mass had to be distributed so that when the pan turned the two points always fell together. Then the two pieces of apparatus were brought into the balance, when the mechanism acted so that they were always placed in the same position on the balance pans. They could also be placed in the same position turned through 180° . If they had been arranged centrally the weighings in the two positions agreed very well. If the masses were not distributed symmetrically, on the other hand, differences of nearly 0.1 m.grm would appear, but in this case satisfactory results could be obtained if the two pieces of apparatus were placed in each of the two positions, and the mean of the four weighings taken. This will be treated more fully in the detailed article.

Other influences, such as electrical or magnetic, were not taken into consideration.

5. Errors caused by the Reaction Vessels.

These might be due to the following causes:—

(a) *Warming of the Vessel when the Reaction Occurred.*—The mixing of the substances was never performed suddenly, but in small portions, lasting two days. However, sometimes a rise of temperature of 5° to 7° was unavoidable. This might give rise to, firstly, an increase in the volume of the vessel, which possibly would not return to its original volume on cooling, and, secondly, a decrease of the water-film on the outer glass surface. As the vessel would lose weight for both these reasons, this was perhaps the simplest explanation of the many decreases of weight which have been observed in chemical reactions, and hence the effect of the warming had to be examined more closely. For this purpose one of two pieces of apparatus which had been weighed many times was placed in an air-bath heated to 30° or 40° for a quarter to one hour, and then after two days again weighed. Many experiments performed during my earlier work and again now showed that, even with this much greater warming, practically no alteration of weight could be proved. The proofs are given in the detailed article. Heydewiller (Drude, *Ann. d. Phys.*, v., 402, 403) has obtained the same result.

As regards the so-called water film on the outer surface of the glass, consisting of glass solution, condensed oil vapours from the machined parts of the balance, and particles of dust, the weight of it upon the surface of the Π -vessels, which amounted to 370 sq. c.m., lay between 0.133 and 0.182 m.grm. With the same sized but much less hygroscopic quartz vessels, it amounted to only 0.037 to 0.082 m.grm. These numbers were obtained from the loss of weight which an apparatus which had remained for several weeks in the balance suffered if it was wiped with a cambric cloth moistened with alcohol.

As in the reaction experiments two vessels of exactly the same surface were always used, the weights of the water film could not differ, and the constancy of the weights of the same apparatus when weighed for weeks showed that the alteration of it resulted in the same way from differences in the amount of moisture in the air.

(b) *Alteration of Volume of the Vessels caused by Alterations of Pressure inside them.*—The chemical reactions performed are always accompanied by a change of volume of the total mass, which is a decrease if from liquids solids separate, and *vice versa*. Thus, when a reaction occurs between silver sulphate and iron sulphate in aqueous solutions of the concentrations used, a decrease of the volume of the masses of the liquids occurs, amounting to 1.67 per cent. (Calculated from the densities of the solid substances and solutions before and after the changes). If the substance introduced into one apparatus besides the water has a volume of 300 c.c., this is reduced to 295 c.c. during the reaction, and if 100 c.c. of air at 760 m.m. pressure were above the liquid, the pressure would sink to 724 m.m. In order to find what effect such alterations of pressure exert on the walls of the Π -tubes, which were 0.75 to 0.8 m.m. thick, a special apparatus of the same glass was prepared. This consisted essentially of a closed cylindrical vessel of cubic contents 400 c.c., surrounded by a glass envelope filled with water which led to a narrow graduated tube. When the air in the inner cylinder is condensed or rarefied, the alteration of volume can be very plainly seen by the movements of the water in the tube, and many different methods showed that for each 100 m.m. increase or decrease of the pressure the original volume of 400 c.c. increased or decreased by 0.0036 c.m. As in the reaction experiments the variation of pressure never amounted to 100 m.m., the volume in the vessels altered so little that no error was to be feared in the weighing.

Some other possible causes of error which were investigated may now be discussed shortly. Thus, the fact that spots and sometimes flakes containing potassium cyanide appear on galvanically gilded brass surfaces owing to oxidation, induced me to examine for alteration in weight the gilded stands used to support the Π -vessels. It was found that the weight remained perfectly constant. As, moreover, as I have already mentioned some vessels filled with the reaction liquids showed decreases of weight on continued weighing without any apparent reason, I investigated whether possibly the particles of water slowly penetrated the thin glass wall. For this purpose one of the two vessels was filled with water and the other with paraffin-oil, and the differences in the weights determined during a period of three months. It was found that the vessel containing water became no lighter.

Almost all the sources of error enumerated have more or less influence upon the final result of the weighing, but they cannot be taken into account separately. In order to get some idea of their total effect a special series of observations was necessary, consisting in filling two vessels with quite indifferent substances, and subjecting them to the same operations and weighings as those filled with the reacting substances. This would give the error affecting the whole method. The first group of the following results deals with the determination of this error.

(To be continued.)

Researches on Azoics. Transformation of the Orthocarboxyl Azoics into Chloro-oxyindazylic Derivatives.—P. Freundler.—The author has recently proved that the azoics which possess an ortho-substituted alcohol or aldehyde function can be transformed with the greatest ease into the corresponding indazylic derivatives. An investigation of azoics with an ortho-substituted radicle affords a still more curious example of this type of reaction. The author's experiments show the existence of an indazylic radicle on the one hand, and the presence of the OH group on the other hand.—*Comptes Rendus*, cxlii., No. 21.

A REVISION OF THE ATOMIC WEIGHTS OF
SODIUM AND CHLORINE.*

By THEODORE WILLIAM RICHARDS
and
ROGER CLARK WELLS.

(Concluded from p. 280).

THE NEW ATOMIC WEIGHTS OF SODIUM AND CHLORINE,
AND THEIR EFFECT ON OTHER ATOMIC WEIGHTS.

FROM the preceding description of the syntheses of argentic chloride, it is clear that 100·000 grms. of the purest metal yields 132·867 grms. of chloride. If then the atomic weight of silver is taken as 107·920† (a convenient value to assume for preliminary calculation), the molecular weight of argentic chloride becomes by simple proportion 143·393, and by difference the atomic weight of chlorine becomes 35·470.

(In this connection it should be pointed out that Leduc called attention to the fact that if Stas's silver really contained as much oxygen as Dumas said it must, chlorine would become 35·47; *Comptes Rendus*, 1901).

This value is about 0·05 per cent greater than the value announced by Stas; and the change produces a serious effect on a number of atomic weights. It is, of course, impossible to be perfectly certain of the accuracy of the new value, because it may contain concealed within it some entirely unsuspected source of error, but at least it is free from the real mistakes in the earlier work. It was reasonably certain that at least ten more syntheses would be needed to affect the value one unit in the third decimal place, if the further results varied no more widely than those recorded above in the final series. Hence it seems unlikely that chlorine is above 35·471 or below 35·469 if silver is taken as 107·920.

What, now, is the effect of this new value upon the atomic weight of sodium? In the table given on p. 238 it is shown that 100·000 grms. of argentic chloride could be obtained from 40·780 grms. of sodic chloride. If now argentic chloride is taken as 143·390, sodic chloride becomes 58·474, and by subtracting the new value for chlorine, 23·004 is obtained as the new value for sodium.

This is not, however, the only value for sodium which may be calculated from our results. On p. 261 has been given a table showing the results of ten experiments on the comparison of sodic chloride with silver direct, and on p. 276 the results of two more. These determinations were made before we had discovered the best method of obtaining pure silver; but the trace of impurity is allowed for in those tables, and it is safe to conclude that 100·000 parts of the purest silver are equivalent to 54·185 parts of sodic chloride. If, then, silver is taken as 107·920 and chlorine as 35·470, sodium becomes 23·007.

Thus two entirely independent values, calculated from two entirely separate series of experiments, yield respectively the values 23·004 and 23·007 for the atomic weight of sodium. Of these two, the latter is somewhat the more trustworthy, because, as has been said, the occlusion of sodic nitrate by the precipitate does not affect it; hence the mean may be taken as 23·006. This value is probably not more in error than two units in the third decimal place, if silver is 107·920, although of course the same remark applies to it that was made concerning the possible error of the value for chlorine. If silver is taken as 107·930, sodium becomes 23·008, and chlorine 35·473. The new values are, then, as follows:—

	Ag = 107·920.	Ag = 107·930.
Atomic weight of sodium ..	23·006	23·008
Atomic weight of chlorine ..	35·470	35·473

The new value for sodium is nearly 0·2 per cent less than that found by Stas—a percentage error much greater even than that made by him in the case of iodine. It will be

noted that the likely error of the new result is only about a twentieth of the difference between the new result and that of Stas. Some will attach significance to the fact that both the new values bring the elements nearer to the demands of Prout's hypothesis.

These new values affect greatly the figures in the second decimal place of all other atomic weights depending directly or indirectly upon chlorine, sodium, or silver. The number of elements thus affected is so great and the relations so complicated as to render imperative a re-calculation of all atomic weights. Nitrogen, as computed from ammoniac chloride, will be especially affected, the new value approaching more nearly that required by Avogadro's rule than the old. Probably, however, it will be best to delay this systematic re-calculation until a few other new data shall have been obtained—in particular new analyses of potassic chloride, argentic chlorate, the bromides, sulphides, and sulphates, and similar important compounds. Some of these are already under way at Harvard, and others will be undertaken at once.

In conclusion, it is a pleasure to acknowledge our great indebtedness to the Carnegie Institution of Washington, without whose liberal support the present investigation could not have attained its present thoroughness or precision.

SUMMARY.

The investigation consisted of a very careful quantitative study of three ratios—namely, AgCl : NaCl, Ag : NaCl, and Ag : AgCl. The effort was made to test every operation involved in the execution of the experiments. In the course of the work, the following points were developed:—

1. Sodic chloride, obtained from many sources and purified in many ways, always gave the same equivalent weight.
2. Fusion in vacuum of salt already fused in air caused no change in this equivalent weight.
3. Argentic chloride precipitated from aqueous solutions always occludes traces of other substances present, and those traces can not always be eliminated. Very dilute solutions must hence be used in precipitation.
4. The conditions governing the occlusion and release of these impurities were minutely studied, and it was shown that Stas's method of dropping solid salt into a silver solution causes occlusion of salt. Many considerations important in all precise chemical work are discussed.
5. A careful study of the solubility of argentic chloride was made, and the precautions necessary in using the nephelometer in the estimation of traces of chloride and silver were ascertained.
6. Fused argentic chloride probably contains traces of dissolved air, but not enough to affect essentially its weight, since subsequent fusion in vacuum caused no appreciable loss of weight.
7. The most difficult question in the purification of silver was found to be the elimination of the inclosed mother-liquor without introducing other impurities. Fusion on pure lime, first in pure hydrogen and then in a vacuum, is the safest method. Stas's silver must have contained at least as much oxygen as Dumas claimed.
8. In ten experiments, 44·5274 grms. of sodic chloride yielded 109·1897 grms. of argentic chloride.
9. In twelve other experiments, entirely distinct from these, 49·5007 grms. of sodic chloride were found to be equivalent to 91·3543 grms of the purest silver.
10. In ten other experiments, again entirely distinct from the preceding, 82·6689 grms. of the purest silver yielded 109·8395 grms. of argentic chloride. Two very different methods of synthesis were used in this series, and the silver came from various sources, these variations being without effect on the result.
11. If the atomic weight of silver is assumed to be 107·920, sodium is found from the above results to have an atomic weight of 23·006, and chlorine an atomic weight of 35·470.
12. Many other atomic weights are affected, in their second decimal places, by these changes. In particular,

* Published by the Carnegie Institution of Washington, April, 1905.

† F. W. Clarke has for a long time accepted this value, and it is now assumed because it is probably nearer the true value than 107·93.

certain slight anomalies previously noticed in Harvard work are explained by them, and the atomic weight of nitrogen computed from ammonia is brought nearer to the value required by Avogadro's rule. Other anomalies appear in other places, however, and it is clear that many new atomic-weight investigations must be instituted to explain them, with due attention to hitherto unheeded dangers, especially of occlusion.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 7th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MESSRS. E. Feilmann and H. G. Smith were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Robert Anderson, Chester Road West, Sunderland; Reginald William Malyon Gibbs, B.Sc., Hetty Villa, Cam Road, Chesterton, Cambridge; Frederick James Martin, Passagem de Marianna, Minas, Brazil; Herbert Arthur Mills, Waverley, Bloomfield Gardens, Bath; Leonard Edward Beard Pearse, 79, Gordon Road, Ealing, W.; Thomas Ebenezer Pye, West View, Summersdale, Chichester; Frederick John Salmon, c/o Princess Estate and Gold Mining Co., Ltd., P.O. Box 112, Roodepoort, South Africa.

Of the following papers those marked * were read:—

*106. *Ammonium Selenate and the question of Isodimorphism in the Alkali Series.* By ALFRED EDWIN HOWARD TUTTON.

Normal ammonium selenate crystallises differently from the seven rhombic normal sulphates and selenates of the alkalis already investigated, namely, in monoclinic prisms or tables, which are described in detail in the paper. A rhombic form of the salt was once obtained (in 1852) by von Lang, but neither Topsøe nor the author has been able to reproduce it in pure ammonium selenate. The author has obtained rhombic mixed crystals of ammonium selenate and sulphate, however, and concludes that ammonium selenate is dimorphous, and that the whole series of sulphates and selenates is probably isodimorphous, as has been shown to be the case with other series of the salts of ammonium, potassium, rubidium, and caesium.

The original crystals investigated by Prof. von Lang have been kindly sent by him to the author, who finds that the majority are truly rhombic, but that they are somewhat impure, containing admixed sulphate, which is probably the reason for their production, for they closely resemble the author's mixed crystals, although much richer in selenate. Besides the rhombic crystals, however, some needles were found of nearly pure ammonium selenate, which are identical with the author's monoclinic form.

The monoclinic crystals of ammonium selenate show a pseudohexagonal primary prism zone very similar to that of the rhombic crystals of the other salts, and the topic parameters calculated on this analogous mode of description show a mean value for the structural dimensions intermediate between the mean value for rubidium and caesium selenates. The molecular volume, refractive indices, dimensions of the optical ellipsoid, and the molecular optical constants are singularly near what would have been expected if the crystals had been truly isomorphically rhombic, and unite in exhibiting ammonium selenate in its proper position in the series immediately after rubidium selenate, precisely analogous to the position of ammonium sulphate in the sulphate series, and which the author has shown is the general position of ammonium crystallographically in the alkali series.

As a side issue, a general explanation has been arrived at for the beautiful optical property of crossed-axial-plane dispersion of the optic axes, ammonium selenate forming the fifth case of this somewhat rare phenomenon which has been met with in the alkali series.

*107. *The Vapour Pressures of Binary Mixtures, Part I. The Possible Types of Vapour Pressure Curves.* By ARTHUR MARSHALL.

The curves showing the variations of partial pressures with molecular composition may be classified into four types, of which three relate to substances which are miscible in all proportions, and are distinguished one from the other according as p/p_1 , the partial pressure divided by the molecular proportion, is less than, equal to, or greater than the vapour pressure of the pure substance. The corresponding total pressure curves are obtained by adding together the two partial pressure curves, which are of the same type. By differentiating the equation of Duhem and Margules, $x d \log p_1 + (1-x) d \log p_2 = 0$, it has been found possible to classify the total pressure curves into twelve types, all of which are known to occur.

It may be proved that with pairs of substances which are miscible in all proportions only one maximum or minimum can occur in the curve of total pressure. The rule, called by Duhem "Regnault's Law," that in the case of partially miscible liquids the total pressure of the heterogeneous mixture is equal to the vapour pressure of the more volatile constituent in the pure state, has been shown experimentally to be approximately true for methyl acetate and water as well as for ether and water, but it is only a rough approximation and is applicable only to some cases.

The vapour pressures of the following pairs of liquids have been investigated experimentally:—nitroglycerol and acetone, diethylamine and acetone, ethyl alcohol and methyl ethyl ketone, water and methyl ethyl ketone, water and methyl acetate, water and ether, water and amyl alcohol. From the curve of total vapour pressures, the partial pressures may be obtained by a simple graphical method.

*108. *The Behaviour of Acetylene with Electrical Discharges of High Frequency.* By HERBERT JACKSON and DUDLEY NORTHALL LAURIE.

The authors have studied the change, observed by one of them some years ago, when acetylene is subjected to discharges from an ordinary high frequency apparatus. A semi-solid, brown substance is formed, which sets to a hard and very insoluble solid on exposure to air. If care be taken to avoid secondary reactions by too prolonged a passage of the discharge, the composition of the solid agrees with that of acetylene, and is apparently a polymericide. The substance absorbs oxygen readily up to about 8 per cent. When heated out of contact with air, an oil distils and a small quantity of gas is evolved, which consists mainly of methane and hydrogen. The authors are proceeding with the examination of the reactions of the substance, which exhibits many curious properties.

*109. *The Behaviour of the Vapours of Methyl Alcohol and Acetaldehyde with Electrical Discharges of High Frequency.* By HERBERT JACKSON and DUDLEY NORTHALL LAURIE.

The authors have examined the reactions as part of a series of experiments conducted with a view to determining the nature and order of change effected by high-frequency discharges when passed through various gases and vapours. Working with discharges of very short duration, they find the first change in the vapour of methyl alcohol to be the formation of carbon monoxide and hydrogen; in the case of acetaldehyde, the greater part of the vapour breaks up into methane and carbon monoxide, but acetylene and water are also produced simultaneously, though in smaller quantities. Both these changes are reversible, the latter more readily than the former. The authors have continued experiments conducted by one of them some time ago on

a number of saturated and unsaturated compounds, and they have come to the conclusion that in the case of paraffin derivatives the general tendency is for unsaturated bodies to give polymeric varieties under the influence of high-frequency discharges, whilst saturated compounds, under similar conditions, yield substances of simpler structure.

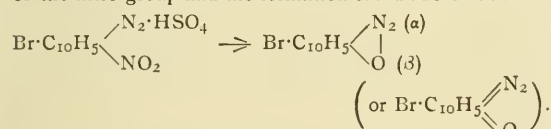
DISCUSSION.

In reply to the President:—Prof. JACKSON said that after trying acetylene made from varying sources, purified acetylene made from calcium carbide and a saturated solution of sodium carbonate was used. The gas was dried over phosphorus pentoxide. No process which could be considered as likely to depolymerise the product gave any acetylene.

In reply to Dr. M. O. Forster:—Prof. JACKSON called attention to the marked activity of the oxidised product obtained after exposing the tacky substance freely to air, and stated that the usual methods for examining for activity in the combined oxygen gave no positive results.

110. "Note on 4-Bromo-2-nitro-1(a)-naphthylamine." By RAPHAEL MELDOLA and HUGH GORDON DALE.

It was shown some years ago by one of the authors and C. H. Desch (*Trans.*, 1892, li., 765) that the above compound could be diazotised under the usual conditions with the formation of diazonium salts which were stable in the presence of excess of sulphuric acid and in cooled solutions. In repeating the diazotisation of the base for another purpose, the authors have found that if the solution of the diazonium sulphate is diluted with water and warmed, an immediate decomposition takes place with the elimination of the nitro-group and the formation of a diazo-oxide:—



This compound is therefore isomeric with the diazo-oxide described by one of the authors and F. W. Streatfeild in 1895 (*Trans.*, lxxvii., 907) and is identical with the compound more recently described by K. J. P. Orton (*Proc.*, 1902, xvii., 253), with which it agrees in melting point (132°) and other properties.

0.0759 gave 7.3 c.c. moist nitrogen at 11° and 765 m.m. N = 11.46. C₁₀H₅ON₂Br requires N = 11.25 per cent.

The chief point of interest attaching to the present mode of formation of the compound is that it is produced by the elimination of the β-nitro-group, instead of by the displacement of the β-halogen atom, as in Orton's process.

The diazo-oxide on boiling with cuprous chloride solution is converted into 1-chloro-4-bromo-2(8)-naphthol, which crystallises from dilute alcohol in white needles melting at 112° and becoming yellowish-brown on exposure to the air.

0.0851 gave 0.1022 AgCl + AgBr. C₁₀H₆OClBr requires 0.1026 AgCl + AgBr.

Special interest attaches to this chlorobromonaphthol in connection with the replaceability of the second β(=3) hydrogen atom, from which point of view the compound may be worth detailed study. Attempts to prepare the 1-chloro-4-bromo-2 : 3-naphthaquinone have so far led to negative results, but the experiments will be repeated under different conditions.

111. "Dinitroanisidines and their Products of Diazotisation." (Second communication). By RAPHAEL MELDOLA and FRANK GEORGE C. STEPHENS.

By the nitration of diacetyl-*m*-aminophenol, the authors have obtained a mixture of two isomeric mononitroacetaminophenols, which, on hydrolysis, yield respectively 4-nitro-3-aminophenol (m. p. 185—186°) and 6-nitro-3-aminophenol (m. p. 158°). The nitro-acetaminophenols on nitration both yield the same dinitro-derivative,

4 : 6-dinitro-3-acetaminophenol (m. p. 168°), and this hydrolyses to 4 : 6-dinitro-3-aminophenol. The latter crystallises in dull orange needles of m. p. 231°. The methyl ether (= 4 : 6-dinitro-*m*-anisidine) obtained by direct methylation, or, more advantageously, by the direct nitration of *m*-acetaminophenol methyl ether, crystallises in small, canary-yellow needles of m. p. 208° (acetyl derivative, m. p. 146°). This dinitro-*m*-anisidine does not lose a nitro- or methyl-group on diazotisation, but forms diazonium salts of the ordinary type. From this, combined with former results, the authors conclude that the conditions essential for the elimination of a nitro-group on diazotisation are that there should be a nitro-group, ortho- or para- with respect to the diazonium group, and that this displaceable nitro-group should have a similar group (or possibly a halogen atom) in the ortho-position with respect to itself. Experiments with other dinitro- and haloid-nitroanisidines are in progress.

112. "The Action of Sulphur Dioxide and Aluminium Chloride on Aromatic Compounds." By SAMUEL SMILES and ROBERT LE ROSSIGNOL.

The authors have previously shown (*Trans.*, 1906, lxxxix., 696) that thionyl chloride reacts with phenetole in the presence of aluminium chloride, giving rise successively to a sulphoxide and a sulphonium base; it has since been found that this reaction may be brought about by sulphur dioxide with the aid of the same condensing agent. An examination of the behaviour of various phenolic ethers towards these reagents has shown that the products of the reaction vary according to the nature and position of the substituents in the aromatic nucleus, and in some cases it has been possible to isolate the primary product, the sulphuric acid, in considerable quantity. Preliminary experiments have indicated that the aromatic hydrocarbons are attacked in a similar manner.

113. "Action of Sodium on *aa*-Dichloropropylene." By IDA SMEDLEY.

Van Romburgh and van Dorssen have shown (*Proc. K. Acad. Wetensch. Amsterdam*, 1905, viii., 565) that the simplest hexatriene, CH₂:CH:CH:CH:CH:CH₂, may be synthesised by heating the diformate of *s*-divinyl glycol.

During the past year, the author has endeavoured to prepare a series of hexatrienes from *aa*-dichloropropylene and its homologues. A preliminary account of these experiments is now put forward.

Hübner and Genthner state that *aa*-dichloropropylene is indifferent to sodium (*Annalen*, 1860, cxiv., 36). The author finds that if a solution of this substance in petroleum (b. p. 100—110°) is heated with potassium or sodium on a water-bath at about 80° during several days and the petroleum solution separated and fractionally distilled, a small amount of a liquid boiling at 60° and a still smaller quantity of a fraction boiling at about 80° can be isolated. A relatively large proportion of a brown, amorphous solid, insoluble in petroleum or water, is also formed in this reaction.

The fraction boiling at 60° gave the following results on analysis:—

C = 87.0, H = 11.85. C₆H₁₀ requires C = 87.81, H 12.19 per cent.

Vapour density found 44, calculated 41.

It united readily with bromine, forming a white, solid tetrabromide melting at 51° and containing 80.02 per cent of bromine. The liquid was therefore diallyl.

The amount of the fraction boiling from 80° to 83° was insufficient for identification; it was probably the hexatriene now isolated by van Romburgh and van Dorssen.

The method is being applied for the reduction of *aa*-dichloro-*γ*-phenylpropylene and of *aa*-dichloro-*γ*-methylpropylene; the substances obtained in these experiments are at present under examination.

114. "Resolution of Lactic Acid by Morphine." By JAMES COLQUHOUN IRVINE.

Fermentation lactic acid may be readily resolved into its

active components by the crystallisation of the morphine salts. On neutralising an aqueous solution of the inactive acid with the alkaloid, the sparingly soluble morphine *l*-lactate separated almost quantitatively, whilst the compound with the *d*-acid remained in solution. The crystalline morphine salt was converted into zinc *l*-lactate, which gave $[\alpha]_D^{20} + 6.84^\circ$ and a more accurate test of the purity of the active acid was obtained by its conversion by means of the silver oxide reaction into methyle *l*-methoxypropionate, which showed $[\alpha]_D^{20} + 94.7^\circ$.

The latter compound was reduced by hydriodic acid to *l*-lactic acid, a reaction which shows that silver oxide does not affect the configuration of an active lactate.

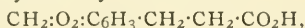
By decomposing the syrup containing the soluble morphine *d*-lactate, more than 50 per cent of the theoretical yield of the active zinc salt ($[\alpha]_D^{20} - 6.83^\circ$) was obtained.

115. "Brazilin and Hamatoxylin." Part VIII. By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

The following synthetical experiments have been commenced with the object of obtaining additional evidence as to the constitution of brazilin and hamatoxylin.

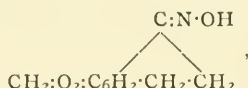
α -Hydrindone, $\text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2$, condenses readily with salicylaldehyde in the presence of caustic potash, and is converted into *salical* - α - hydrindone, $\text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CO}) \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, which crystallises in yellow needles and decomposes at 206° . It yields a brilliant red potassium derivative, but does not appear to combine with hydrogen chloride.

When methylene dihydrocaffeic acid,—



is treated with phosphorus pentachloride and then with aluminium chloride (compare Kipping, *Trans.*, 1894, lxx., 484), it is converted into *methylene dihydroxy* - α - hydrindone,

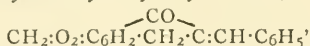
$\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$, which melts at 160° . The oxime,—



obtained by the action of hydroxylamine hydrochloride and caustic potash in the usual manner, melts at 246° with decomposition. *isoNitrosomethylenedihydroxy* - α - hydrindone,

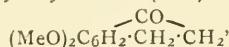
$\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CO}) \cdot \text{N}\cdot\text{OH}$ is formed when an alcoholic solution of methylenedihydroxy - α - hydrindone is mixed with *iso*amyl nitrite and hydrochloric acid. It crystallises in yellow needles, decomposes at 230° , and when treated first with phosphorus pentachloride and then with caustic potash, yields *methylenedihydroxyhomophthalic acid*, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_2(\text{CO}_2\text{H})\text{CH}_2 \cdot \text{CO}_2\text{H}$, which crystallises from water and melts at about 236° .

Benzalmethylenedihydroxy - α - hydrindone,—

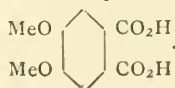


is produced when methylenedihydroxy - α - hydrindone is treated with benzaldehyde and alcoholic potash, and crystallises in pale yellow needles which decompose at about 250° .

4 : 5-Dimethoxy - α - hydrindone (1 : 2),—

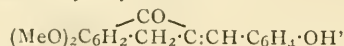


is obtained when dimethyldihydrocaffeic acid, $(\text{MeO})_2\text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is treated with phosphorus pentachloride and then with aluminium chloride. It crystallises from benzene, melts at 114° , and, when oxidised with nitric acid, yields *m*-hemipinic acid,—



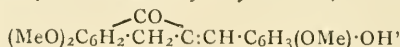
The *isonitroso*-derivative, $(\text{MeO})_2\text{C}_6\text{H}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CO}) \cdot \text{N}\cdot\text{OH}$, crystallises in yellow needles which decompose at about 240° .

Salicaldimethoxy - α - hydrindone,—



is produced when dimethoxy - α - hydrindone is treated, in alcoholic solution, with salicylaldehyde and caustic potash. It crystallises in yellow needles, yields a brick-red hydrochloride, and a brilliant red crystalline potassium derivative.

p-Methoxysalicaldimethoxy - α - hydrindone,—



is of special interest on account of the close relationship which it bears to trimethylbrazilin. It is obtained when dimethoxy - α - hydrindone is treated with *p*-methoxysalicylaldehyde and caustic potash in alcoholic solution, and crystallises from *iso*amyl alcohol in prisms which decompose at about 230° . It yields a golden yellow potassium derivative and a crimson hydrochloride.

The authors are engaged in the further investigation of the above and other analogous substances.

116. "A Study of the Reaction between Hydrogen Peroxide and Potassium Persulphate." By JOHN ALBERT NEWTON FRIEND.

It is shown that solutions of hydrogen peroxide and potassium persulphate interact according to the equation $\text{H}_2\text{O}_2 + \text{K}_2\text{S}_2\text{O}_8 = 2\text{KHSO}_4 + \text{O}_2$. The reaction, however, is monomolecular. This is due to the formation of an intermediate and highly unstable compound, directions for the preparation of which are given. Sulphuric acid is found to exert a retarding influence on the reaction, as do the sulphates of sodium, potassium, and manganese, the last named accelerating slightly as the reaction nears completion. The action of colloidal platinum has also been studied.

117. "The Action of Magnesium Methyl Iodide on Dextrolimonene Nitrosochlorides." By WILLIAM AUGUSTUS TILDEN and FREDERICK GEORGE SHEPHERD.

The α - and β -nitrosochlorides were treated separately, but yielded similar products differing only in melting point and degree of optical activity. The compound formed in each case differs in composition from the nitrosochloride by one atom of oxygen, and therefore has the formula $\text{C}_{20}\text{H}_{32}\text{ON}_2\text{Cl}_2$. It is insoluble in aqueous alkalis and in acids, though easily soluble in the usual organic solvents. Alcoholic potash removes the elements of hydrogen chloride, but the resulting oil rapidly changes in contact with the air. No definite derivatives could be obtained by the use of any reagent except phosphorus pentachloride, which replaces the remaining atom of oxygen by two atoms of chlorine. The product, $\text{C}_{20}\text{H}_{32}\text{N}_2\text{Cl}_4$, is optically active and readily loses two molecules of hydrogen chloride, yielding the compound $\text{C}_{20}\text{H}_{30}\text{N}_2\text{Cl}_2$, which is also optically active and saturated. The product of the action of phosphorus pentachloride does not react as a nitrogen chloride.

118. "Electrolysis of Potassium Ethyl Dipropyl Malonate." By DAVID COWAN CRICHTON.

A concentrated aqueous solution of potassium ethyldipropylmalonate yields on electrolysis the ethyl esters of α -propyl- β -ethyl-acrylic acid, dipropylglycollic acid, tetrapropylsuccinic acid, and probably dipropylacetic acid.

The dipropylglycollic acid obtained in the electrolysis was proved to be identical with the "dipropylloxalic acid" of Rafalsky.

Tetrapropylsuccinic acid yields an anhydride which is characterised by the same stability towards alkalis as tetraethylsuccinic anhydride.

119. "A New Method for the Measurement of Hydrolysis in Aqueous Solution, based upon the consideration of the Motion of Ions." By ROBERT BECKETT DENISON and BERTRAM DILLON STEELE.

The authors have previously described a method for the direct determination of transport numbers and ionic velocities which necessitates the employment of an auxiliary or indicator solution. This indicator must not be hydrolysed if accurate results are to be obtained, since hydrolysis causes the production of new ions which have an effect on the apparent velocity of the ion which is being subjected to measurement. Thus, if lithium chloride is used as an indicator for potassium chloride, correct numbers for the velocity of the K⁺ ion are obtained, since lithium chloride is not hydrolysed in solution. If, however, a salt of the nature of aniline hydrochloride is used as indicator, the H⁺ ions which are produced as the result of hydrolysis cause a false value to be obtained for the velocity of the K⁺ ion. The difference between the real and apparent velocities of the K⁺ ion is dependent on the degree of hydrolysis of the indicator, and it has been found possible, by means of a study of the motion of the different ions in the system, to deduce a formula which gives values for the degree of hydrolysis in the indicator solution well in accordance with the numbers commonly accepted as correct. The only measurements which have to be made are three conductivity determinations. Measurements have been carried out with three salts, namely, the hydrochlorides of aniline, *ortho*- and *para*-toluidine at 18° and 25°. The values obtained for the "hydrolysis constants" are:—

	Aniline hydrochloride.	<i>o</i> -Toluidine hydrochloride.	<i>p</i> -Toluidine hydrochloride.
At 18°	61.9 × 10 ³	46.0 × 10 ³	256 × 10 ³
At 25°	43.6 × 10 ³	29.6 × 10 ³	186 × 10 ³

This gives for the "dissociation constants" of the respective bases (assuming for water H⁺ × OH⁻ = 1.2 × 10⁻¹⁴) at 25°:—Aniline = 5.2 × 10⁻¹⁰; *o*-toluidine = 3.5 × 10⁻¹⁰; *p*-toluidine = 2.2 × 10⁻¹⁰.

From the values obtained for the "hydrolysis constants" of the hydrochlorides at 18° and 25°, the heat of hydrolysis was calculated by the application of van't Hoff's equation. The results were in fair agreement with the values obtained calorimetrically, the numbers being as follows:—Aniline hydrochloride, 8700 cal.; *a*-toluidine hydrochloride, 11,000 cal.; *p*-toluidine hydrochloride, 7900 cal.

120. The Oxidation of Hydrocarbons by Ozone at Low Temperatures." By JULIEN DRUGMAN.

Experimental proof is given that the mode of action of ozone on a saturated and an unsaturated hydrocarbon is very different.

Ozone acts, at the ordinary temperature, very slowly on saturated hydrocarbons such as methane and ethane. The process is one of gradual hydroxylation. In the case of ethane, ethyl alcohol is shown to be the first product formed.

The reaction in the case of an unsaturated hydrocarbon such as ethylene is instantaneous, even at temperatures far below 0°.

A very explosive addition compound is first formed, which decomposes extremely readily, giving oxidation products containing only one carbon atom. The carbon chain is broken at the double bond.

Comparison with the results of Harries' work make it probable that the addition product is an ozonide, but the decomposition of this is more complex than that usually obtained with a liquid or solid ozonide. The following equations probably represent the process:—

- (1). C₂H₄ + O₃ = C₂H₄O₃ = { $\begin{matrix} (a) & \text{CH}_2\text{O} + \text{HCO}_2\text{H} \\ (b) & \text{CH}_2\text{O} + \text{CO} + \text{H}_2\text{O} \end{matrix}$ }
- (2). C₂H₄O₃ + H₂O = 2CH₂O + H₂O₂.

Formaldehyde, formic acid, carbon monoxide, hydrogen peroxide, and water are obtained.

121. "Reactions Involving the Addition of Hydrogen Cyanide to Carbon Compounds. Part V. Cyanodihydrocarvone." By ARTHUR LAPWORTH.

The nitrile formed when carvone unites with one molecular proportion of hydrogen cyanide (Hann and

Lapworth, *Proc.*, 1904, xx., 54), is cyanodihydrocarvone, CHMe<math display="block">\begin{matrix} \text{CO} & \text{CH}_2 \\ | & | \\ \text{CH}(\text{CN}) & \text{CH}_2 \end{matrix}>\text{CH}\cdot\text{CMe}:\text{CH}_2, and the two acids to which it gives rise on hydrolysis are the corresponding stereoisomeric carboxylic acids. Evidence of the occurrence of reversible dynamic isomerism in the nitrile and the two acids has been obtained.

The properties of these compounds and of a number of their derivatives are described.

122. "Thiocarbamide as a Solvent for Gold." By JAMES MOIR.

Two new complex gold-salts have been obtained by dissolving gold in an acid solution of thiocarbamide (*Proc.*, 1906, xxii., 105). They approximate in composition to Au₂SO₄ + 6CH₄N₂S and AuCl + 2 $\frac{3}{2}$ CH₄N₂S respectively, but the author considers that the correct formulæ are C₆H₂₀N₁₂S₆Au₂(SO₄) and C₈H₂₆N₁₆S₈Au₃Cl₃ respectively,

and that both contain a complex cation C₂H₆N₄S₂Au⁺ [most probably NH:C(NH₂)·S(Au)·NH·CS·NH₂ +]. The author

suggest that the abnormal cuprous-thiocarbamide salts have similar constitutions.

The chloride has been studied in some detail. It is converted into the compound described by Reynolds, C₂H₈N₄S₂AuCl, by boiling with hydrochloric acid. Its formation from aurichloride and thiocarbamide takes place according to the equation:—



On warming with sodium hydrate solution, it gives the olive-green gold compound described by B. Rathke (*Ber.*, 1884, xvii., 307), which the present author formulates as CH₃N₂S₂Au₃; the filtrate contains chloride and sulphide of sodium. On heating to 210° until constant, the brown residue appears to have the composition Au₃S₂·3CH₄N₂S.

Silver nitrate gives a mixture of silver chloride, auric hydrate, and silver thiocarbamide in the proportions required by the formula assigned to the original substance.

Substituted thiocarbamides have no action on gold.

123. "An Improved Beckmann Apparatus for Molecular Weight Determinations. By JAMES MCCONNELL SANDERS.

In the determination of molecular weights by the freezing-point method, employing the Beckmann apparatus as usually constructed, several sources of error have to be contended with, some of which depend on the form of the apparatus, and are considerably augmented when hygroscopic solvents such as acetic acid are used.

One of the chief difficulties is to equalise the overcooling for parallel observations with the solvent and solution, and it is not always easy to add the ice crystals which induce congelation at correspondingly equal temperature intervals from the freezing-point. With the little contrivance ("Impfstift") recommended by Beckmann for this purpose, several errors are liable to be introduced; an unknown, or at least a variable, addition to the weight of the solvent is made, the ice crystals absorb moisture during their transference, and during the time that the side tube is open, moisture is absorbed by the solvent in the tube.

Moreover, when the temperature of the surrounding atmosphere is but a few degrees above the freezing-point of the solvent, it is difficult to ensure the addition of the crystals to the solvent or solution at the precise moment when they are required. Another source of error exists in the introduction of moist atmospheric air by the action of the stirrer.

The author has succeeded in eliminating these errors by the use of the modified form of inner tube described in this paper.

The principal feature of the new inner tube consists in the use of the narrow, almost capillary side tube, A, which is fused into the bottom of the solution tube, and is carried up and bent so as to permit the attachment of a thin rubber tube and small bulb, B. When the solvent has been placed in the containing tube, the height of the column of liquid in A can easily be adjusted by first expelling it com-

pletely by compression of B, then pinching the rubber tube while B is removed, allowed to fill itself with air, and replaced. On releasing the rubber tube a small amount of the solvent rises in A, and the height of the column subsequently increases owing to the contraction of the air in the tube produced by the cooling. The container tube is placed in a wide jacket tube (not shown in the figure) in such a way that the side-tube, A, is in contact with the walls of the latter; a better arrangement is to employ a tube with a lateral canal such as is provided in some hydrometer cylinders.

In operation, the column of solvent in A, being nearer to the source of cold, freezes first, and at the moment desired a mass of crystals can be projected into the main body of the solvent by a sharp compression of the bulb, B.

The pneumatic stirrer, C, is almost self-explanatory; it is an adaptation of the well-known pneumatic "shutter release," found on the majority of photographic cameras. The piston and cylinder are of aluminium or glass ground to fit perfectly (in the author's laboratory use was made of a glass hypodermic syringe of small diameter), the agitator, E, is made by flattening a portion of the length of a piece of platinum wire, and then twisting the flattened portion in the manner shown; the twisted part is coiled into a spiral form, and the other end of the wire fixed to the end of the plunger or piston. The spring which balances the weight of the agitator is made of hard drawn aluminium or platino-iridium wire, sufficient length being given to it to allow of a somewhat extended "stroke."

One of the conveniences attending this arrangement lies in the fact that both stirrer and "crystallisation inducer" can be easily operated without the fatigue attendant on the use of the ordinary form; the operator's hands rest on the table, and he can conveniently observe the thermometer without his attention being distracted by manipulative details.

The ordinary side-tube of the Beckmann apparatus is replaced by the small vertical tube, D, which passes through a third perforation in the rubber stopper. The introduction of the substance can be accomplished by the momentary removal of the stopper of D, or if it should be desired to avoid all possibility of the entrance of atmospheric air, the substance in the form of a compressed tablet can be previously placed in D, and sustained by a bent wire, G, a half revolution of the latter allowing the tablet to drop into the solvent at the desired moment.

The apparatus can easily be constructed by anyone accustomed to glass working, or it can be adapted from a small Soxhlet extraction tube by cutting off the upper and lower parts, and the wide side tube, and bending the narrow syphon tube into the form of A.

(We are indebted to the author for permission to insert the woodcut illustrating the paper).

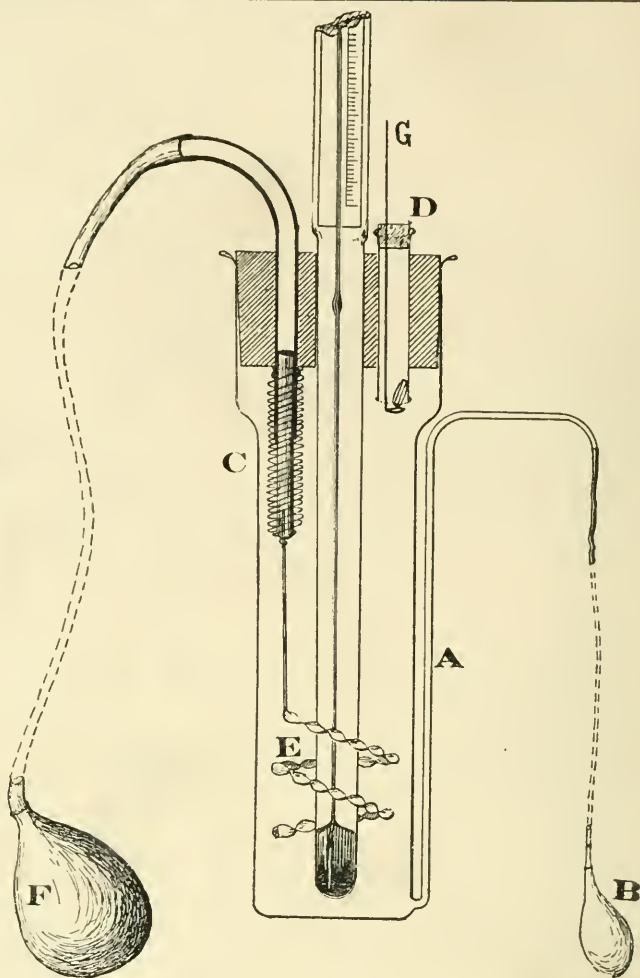
PHYSICAL SOCIETY.

Ordinary Meeting, June 8th, 1906.

Prof. J. PERRY, F.R.S., President, in the Chair.

A PAPER by Mr. H. DAVIES, "On the Solution of Problems in Diffraction by the Aid of Contour Integration," was read by the Secretary.

This paper is an attempt to obtain a solution of diffraction problems by means of contour integration. The method adopted is to obtain a solution for unbounded



space as a contour integral. The special boundary conditions are then accounted for by adding terms to the previous expression. When the complete expression has been obtained it is then evaluated in the form of a series by the aid of Cauchy's Residue Theorem. The special case of a wedge of angle less than 2π and with the light vector parallel to the edge of the wedge is solved in the present case.

Mr. J. GOULD'S Experiments with a Vibrating Steel Plate were exhibited by Messrs. Newton and Co.

The phenomena peculiar to this plate may be classified under two heads.—(1) Beats, simultaneously audible and visible; (2) dispersion figures. In addition to these, vortex-vibration, resonance-effects, and many other experiments may be exhibited by using suitable clamps, &c. The dispersion figures are due chiefly to the interaction of two systems of vibrations of the same pitch working at right angles to each other. These two vibration systems may be distinguished as D and L. D is the second of a series of transverse systems in all of which the plate is divided into two equal parts by one nodal line running from end to end, and by one or more nodal lines across the width; in the case where there are two cross lines they are almost identical in position with the two lines proper to the fundamental vibration. But whilst the pitch of the fundamental system is about 70 vibrations per second, that of the D

system is nearly 700. The L system is the first, or lowest, lateral vibration, the direction of vibration being across the width of the plate. These two systems being tuned closely to the same pitch (by means of suitable clamps), careful manipulation with a synchronising rubber will cause any light powder scattered on the plate to be thrown on to the nodal lines proper to D. Strong excitement will, however, immediately bring the L system into activity; the nodal lines will be broken up, and the scattered particles roll to and fro in waves and torrents of great variety, according to the varying distribution of energy between the two vibration systems. Instead of strongly exciting D only, gentle touches of varying intensity may be applied to both systems, according to the effects desired. Dispersion-figures are neither node-figures nor vibration-figures, but, in a sense, they are both, inasmuch as they are perturbations of node lines due to the action of fluctuating vibration. Node-figures are the boundaries of single systems of vibration. Dispersion-figures are resultants of the interaction of at least two systems. Node-figures are fixed; dispersion-figures are fluent, but may be fixed at any stage by stopping the vibration with sufficient promptitude. The principles involved in this phenomenon are identical with those that determine the action of Wilberforce's Spiral Spring. In both cases there is an alternating transfer of energy, by cumulative action, between two synchronising systems of vibration operating at right angles. The principles are identical, but the conditions are very diverse. The spring makes, say, one vibration per second, the plate 700. In the spring action the whole energy is transferred from vertical to horizontal, or *vice versa*, in about 30 vibrations; in the plate action the parallel transfer may require five or six thousand vibrations. With regard to manipulation of the plate, when the interval between the two systems is extremely small, it is almost impossible to excite one without bringing the other into action; in fact, whichever gets the start may be excited through the other. In other words, the manipulation proper for the excitation of one is liable to produce excitation of the other. Beats are most decisive when there is a distinct interval between the two vibration systems; a difference of about 3 or 4 vibrations per second is generally most effective. In this case it is necessary to excite both systems separately so as to obtain vibrations of equal amplitude.

A paper on "Fluid Resistance" was read by Col. R. DE VILLAMIL.

Prof. Hele-Shaw, in a paper on "The Motion of a Perfect Fluid," remarks that one of the most perplexing things in engineering science is the absence of all apparent connection between the higher treatises on hydrodynamics and the vast array of works on practical hydraulics. The reason for this appears to be the immense difference between the flow of an actual liquid and that of a perfect one, owing to the property of viscosity. According to the author this is not the only reason. There appear to be two fundamental difficulties to be got rid of before they can be reconciled. Engineers assume that a liquid can be "pushed" in any rectilinear direction. This, though a very popular notion, is not correct. A liquid, like an electric current, can move in one manner and in one manner only, viz., from a region of higher pressure, or potential, to a region of lower pressure. The author examines the action of a small circular blade moving squarely in a liquid, and shows that, however the matter is considered, the blade cannot "push" the liquid or be pushed by it. The other difficulty is the assumption that in a perfect fluid there can be no resistance of any kind to any moving body moving in it in any velocity. It is only in an infinite ocean of perfect fluid that there would be no resistance. Latterly, however, writers have omitted the words infinite ocean, and have laid down that in all cases a perfect fluid would offer no resistance. This there is no evidence to support.

NOTICES OF BOOKS.

The Life and Experiences of Sir Henry Enfield Roscoe, D.C.L., LL.D., F.R.S. Written by Himself. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1906.

THOSE who enjoy biographies and also books with "happy endings," and who can seldom gratify both tastes simultaneously in the perusal of one volume, will be delighted with this account of the life and experiences of Sir Henry Roscoe. The story of his life necessarily includes much of interest about the growth of scientific teaching in England, and the development of Owens College, Manchester, and of the University of London, in connection with which Sir Henry Roscoe did great service to the nation; while the anecdotes of his early student days at Heidelberg and his relationship with Bunsen make lively and, in many cases, amusing reading. His views on the teaching of chemistry, which may be said to show that he belongs in this respect to the older school, are worth careful consideration, as well as his opinions on such subjects as technical education; and the chapters on his work other than scientific force us to recognise that it is indeed seldom that we have the opportunity of reading the life, written by himself, of a man of such many-sided activity and distinguished achievements.

Die Literatur des Vanadins, 1804-1905. By Dr. WILHELM PRANDTL. Hamburg and Leipzig: Leopold Voss. 1906.

THIS collection of publications relating to the chemistry of vanadium and its compounds is a model bibliography, being complete and conveniently arranged. All the more important German and other journals have been carefully searched for the purpose of its preparation, and articles are included in which even isolated and incidental allusions are made to the element or its compounds. Moreover, in all cases translations and abstracts are noticed as well as the originals, so that the compilation must have been a task of considerable magnitude. The arrangement is chronological, and for each article, besides the year of publication and author's name, the full title is given, and, when this does not clearly indicate the scope of the paper, a very brief note pointing out the contents is appended. The book is provided with an index of authors' names, and also a well-classified subject index, which adds greatly to its usefulness.

Flüssige Luft. ("Liquid Air"). By R. NOWICKI and HANS MAYER, Second Edition. Mähr.-Ostrau: R. Papauschek. 1906.

THIS small book gives an interesting account of the liquefaction of gases, more especially of air. The early experiments in this direction are simply and clearly explained, while the various processes now usually adopted in France, Germany, and England are described in detail, the text being well illustrated. The most novel and perhaps the most valuable feature of the book is the collection of experiments which can be performed to demonstrate the properties of liquid air; the directions given are very explicit, and those who are contemplating the delivery of a "popular lecture" will find, if they consult this book, many useful hints on manipulation, and the most striking experiments. The second edition has been revised by Hans Mayer, and the most important modern methods of producing liquid gases are described in it, while the new matter given for the first time includes many fresh experiments, besides additional diagrams.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 21, May 21, 1906.

Sulphides, Selenides, and Tellurides of Tin.—H. Pélabon.—The author determines the temperature of fusion of mixtures, in varying proportions, of tin and one of the non-metals—sulphur, selenium, and tellurium. These mixtures, after being raised to a high temperature, are slowly cooled in such a way that the exact temperature when solidification starts can be determined. The results are represented by curves with abscissæ the proportion of non-metal in the mixture (proportion R being expressed in hundredths of the weight of non-metal to the total weight of the mixture) and ordinates the temperature of solidification.

New Methods of Preparation of certain Organic Derivatives of Arsenic.—V. Auger.—The author investigates easy methods of transformation of the principal methyl derivatives of arsenic, starting usually from methylarsinic and cacodylic acids, which are produced commercially at a moderate price. He succeeds in preparing the following compounds:—Methylarsine iodide, CH_3AsI_2 ; methylarsine chloride, CH_3AsCl_2 ; cacodyle chloride, $(\text{CH}_3)_2\text{AsCl}$; cacodyle, $(\text{CH}_3)_2\text{As}.\text{As}(\text{CH}_3)_2$; and tetramethylarsonium, $(\text{CH}_3)_4\text{AsI}$.

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THE CHEMICAL NEWS.

VOL. XCIII., No. 2431.

THE ESTIMATION OF ORGANIC MATTER WITH PERMANGANATE IN ACID AND IN ALKALINE LIQUIDS.

By C. ALBERTO GARCIA (Instituto de Higiene, Lima, Peru).

THE author comes to the following conclusions:—In the estimation of organic matter with permanganate in an alkaline solution the free ammonia which may exist or be formed in the reagent becomes oxidised and transformed into nitrous or nitric acid, and this increases the expenditure of the permanganate.

Besides the saline ammonia which may be found in the water, the nitrogen of the nitrogenous organic matters liberated in the form of ammonia through the action of the permanganate and of the alkali, whether a bicarbonate or not, increases the expenditure of permanganate, and this explains why larger quantities are obtained in the estimations in an alkaline than in an acid medium when the origin of the organic matters is animal, through the action of the albumenoid ammonia formed.

INVESTIGATIONS ON THE OCCURRENCE OF CHANGES IN THE TOTAL WEIGHT OF SUBSTANCES UNDERGOING CHEMICAL TRANSPOSITIONS.*

(SECOND COMMUNICATION).

By H. LANDOLT.

(Concluded from p. 286).

RESULTS OF THE OBSERVATIONS.

As was explained before, only the final results can be given in this paper, *i.e.*, the alterations in weight obtained in these experiments. These are deduced from the difference of weight of the apparatus A and B—

- I. In a series of weighings before the reaction.
- II. In a series of weighings after the reaction in A.
- III. In a series of weighings after the reaction in B.

Each series consisted of four to eight weighings, and the mean error of the mean of these varied between ± 0.002 and ± 0.008 m.grms. Always denoting the heavier vessel by A, decreases of II. in comparison with I. indicated decrease of weight, and increases showed increases of weight of A. After the reaction in B, weighing III. must again agree approximately with I. Table III. contains also the error in weighing of the result, calculated by summing the mean errors of the two series of weighings.

TABLE III.

Series of weighing.	Difference of weight, A—B.	Mean error.	Result.		
			Vessel.	Alteration of weight.	Error of weighing.
I.	3.588	± 0.003	A	-0.076	± 0.009
II.	3.512	0.006			
III.	3.570	0.005	B	-0.058	0.011

I. Determination of the Total Experimental Error by filling the Vessels with Non-reacting Substances.

The two divisions of the reaction vessels were filled either with the same or with two different indifferent liquids (Expts. Nos. 1 to 7). In other cases (Expts. 8 to

19) the apparatus in which a reaction had already taken place was used, and the previous operation was repeated with the then homogeneous mass contained in it. To replace the missing heat of reaction in several experiments (4, 5; 10, 11), the vessel was placed for some time in an air-bath heated to 30–40°. The results are collected in Table IV. These nineteen experiments lead to the following conclusions:—

The alterations in weight given in Col. VII., which include all the errors appearing during an experiment, are both increasing and decreasing, the + sign appearing eight times and the – sign eleven times. The mean of the sum of the two alterations in both directions amounts to +0.008 and –0.010 m.grm.

Of the nineteen experiments, seventeen gave an alteration of weight of less than 0.017 m.grm. Only in two cases (Nos. 12 and 13) did this rise to 0.023 and 0.024 m.grm., and this last number may be taken as the maximum error affecting the method. If the limit is moved back a little more, and put at 0.03 m.grm., it is perfectly certain that if an alteration of weight exceeding this amount is observed in an experiment it cannot be caused by errors of observation.

The numbers in Col. VII. include:—

(a) The influences to which the vessels are exposed during the whole operation, and those which may arise through different layers of moisture on the outer glass surface, the slightly unequal volumes of the two vessels, alteration of volume in consequence of the heat of reaction, touching with the transport arrangements, deposit of dust, &c.

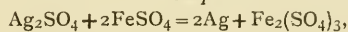
(b) The errors of the balance and the process of weighing. The amount of these is given in Col. VIII., and it is seen to vary between the limits ± 0.006 and ± 0.015 m.grm., thus always remaining much smaller than the total error.

The above maximum error of 0.03 m.grm. relates to the experiments which had been performed since 1901 with the new Rueprecht's balance. As regards the old experiments from the years 1890 to 1892 and 1899, for which Stückrath's and the old Rueprecht's balance were used, and also larger vessels, the mean error of the mean of a series of weighings amounted to ± 0.004 to ± 0.014 m.grm., as the first paper showed. The total experimental error was not determined, but it did not in any case exceed 0.05 m.grm.

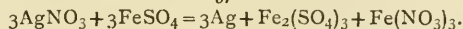
Heydweiller (*Drude's Ann. d. Physik.*, 1901, vol. v., p. 404) estimates the greatest error affecting his observations at 0.04 m.grm.

II. Experiments with Substances capable of Reacting.

First Reaction: Silver Sulphate or Nitrate and Ferrous Sulphate.



or



The two substances were taken in such proportions that the iron vitriol was largely in excess. Nevertheless, as special experiments showed, complete reduction of the two silver salts never took place, but only about 94 to 95 per cent of the total amount of silver separated. When silver sulphate was used, on account of its insolubility, the reduction took place for the most part in the solid state.

The experiments are divided into three groups (Table V.), according to the dates when they were carried out:—

(a) Nos. 1, 2, 3.—Old experiments of the years 1890 and 1892 already described in the first paper. Old Rueprecht's and Stückrath's balance; large η -vessels; weight when filled, about 925 grms.; silver separated, 40 and 60 grms.; error of weighing, up to ± 0.030 m.grm.

(b) Nos. 9, 10, 11.—Experiments of the years 1899 and 1900. Stückrath's balance; large η -vessels weighing about 820 grms.; silver separated, 63.5 grms.; error of weighing, up to ± 0.030 m.grm.

(c) Nos. 4 to 8, 12, 13.—New Rueprecht's balance;

* From *Sitzungsber. d. K. Akademie d. Wissensch.*, 1906, viii., 266.

small Π - or O-vessels; weight when filled, 400 to 540 grms.; silver separated, 16.5, 24, 31 grms.; error of weighing, up to ± 0.010 m.grm.

From Table V. it is seen that—

1. The prevailing phenomenon is a decrease of weight, and in nine experiments (Nos. 1 to 6, 9 to 11) this exceeds the maximum error of observation so much that it cannot be explained thus.

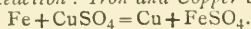
2. Generally speaking, as the reaction mass used or the quantity of silver separated increases, the decrease of weight seems to become greater. If the relation of the decrease is calculated to 100 grms. of silver, the following numbers were found for the nine experiments:—

Expt. No.	Decrease of wt. M.grm.	Expt. No.	Decrease of wt. M.grm.
1.	0.42	6.	0.28
2.	0.33	9.	0.31
3.	0.22	10.	0.22
4.	0.27	11.	0.12
5.	0.43		

If but little strict proportionality appears here, nevertheless there is an approximation to proportionality. The mean would be 0.29 m.grm. for each 100 grms. of silver.

3. Experiments Nos. 7, 8, and 12, 13 in which Π -vessels were used, the inner glass surfaces of which were covered with a layer of solid paraffin, are an exception. In the first two cases the decrease of weight only slightly exceeds the maximum experimental error of 0.03 m.grm., and in the last two the weight actually remained quite unaltered.

Second Reaction : Iron and Copper Sulphate.



As was mentioned in the introduction, this reaction has been investigated by Heydweiller, using Π -tubes, one limb of which was filled with 14 to 18 grms. of iron powder, and the other with an excess of copper vitriol and water. The following differences then appeared:—

(a) When copper sulphate free from acid was used (crystallised from a solution containing some caustic soda) two experiments gave differences of -0.026 and $+0.019$ m.grms., thus no alteration of weight.

(b) If the water used to dissolve the copper vitriol contained a small quantity of alkali, in three experiments the considerable decreases -0.217 , -0.161 , -0.176 m.grm. appeared, which far exceeded the maximum experimental error assumed by Heydweiller, i.e., 0.04 m.grm. Almost equally large alterations, viz., -0.097 and -0.158 m.grm. were obtained on the addition of a small quantity of sulphuric acid to the solution of the copper salt.

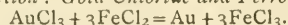
I repeated the experiments, using Π -tube of Jena glass, containing:—

- (a) In Experiments 1 and 2—In one limb, 15.0 grms. piano-string wire + 120 grms. pure water; in the other, 70.0 grms. $\text{CuSO}_4 \cdot 5\text{aq}$ + 65 grms. pure water.
- (b) In Experiments 3 and 4—In one limb, 15.0 grms. iron filings + 125 grms. water containing some drops of NaOH ; in the other, 70.0 grms. $\text{CuSO}_4 \cdot 5\text{aq}$ + 70 grms. water containing some drops of NaOH . (67.0 grms. $\text{CuSO}_4 \cdot 5\text{aq}$ stoichiometrically necessary).

With Rueprecht's new balance the results given in Table VI. were obtained. Thus in all four cases decreases of weight occurred, but they were so small in Nos. 1 and 2 that although they exceeded the error in weighing (in the case of No. 2) nevertheless were within the limit of the maximum experimental error of 0.03 m.grm. In agreement with Heydweiller it is thus shown that when copper sulphate free from acid is used no alteration of weight takes place, a result also obtained by Lo Surdo, as I have mentioned. Experiments 3 and 4, when alkali was added, did not give the large increases of weight which Heydweiller observed. In the case of No. 3 it was within the limit of the maximum experimental error of 0.03 m.grm., and in

No. 4 only slightly exceeded it. Thus the occurrence of a decrease of weight cannot be established with certainty. To decide the question, further experiments are necessary, also those with addition of sulphuric acid.

Third Reaction : Gold Chloride and Ferrous Chloride.



Π -tubes of Jena apparatus glass were used for the experiment. Into one limb was introduced 122 grms. of a solution of gold chloride prepared from 12.032 grms. of gold, and containing 18.521 grms. of AuCl_3 ; and into the other 122 grms. of ferrous chloride solution, which had been prepared by treating 12.00 grms. of pure iron with hydrochloric acid, and contained 27.20 grms. of ferrous chloride. The quantity stoichiometrically necessary would amount to 23.21 grms. The precipitation of the gold was complete, and during the reaction only a very slight development of heat occurred. (New Rueprecht's balance).

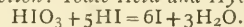
The experiment had to be limited to the vessel A, as B was afterwards damaged.

Date of Experiment : January, 1903.

Gold precipitated (grms.)		12.032
Observed alteration in weight (m.grm.)	..	-0.009
Error in weighing (m.grm.)		± 0.010

According to this, in this reaction no appreciable alteration of weight occurs. But it must be noticed that the experiment was performed with only small quantities of substances.

Fourth Reaction : Iodic Acid and Hydriodic Acid.



As in the earlier experiments, into the one limb, not aqueous hydriodic acid, but a solution of potassium iodide was introduced, and into the other a sufficient quantity of sulphuric acid besides the iodic acid solution. Thus a premature beginning of the action owing to hydriodic acid gas passing over was avoided. The iodic acid was always used in excess.

Table VII. contains, besides six old experiments, seven new ones. It appears at once from this table that in all thirteen experiments a decrease of weight occurred. In eight cases (Nos. 2, 3, 4, 5, 7, 8, 12, 13) this exceeds the errors of observation (old experiments, 0.05 m.grm; new, 0.03 m.grm.) to a considerable extent; in five cases (Nos. 1, 6, 9, 10, 11), on the other hand, it does not exceed the limits of error.

Fifth Reaction : Iodine and Sodium Sulphite.

This reaction, like the foregoing, may be used for the investigation of the question whether the alterations of weight are connected with the dissociation processes. When iodic acid and hydriodic acid react, iodine being separated, electrons disappear, while in the present case they appear; thus, opposite effects were to be expected. My previous four tests of the reaction had, however, given quite contradictory alterations of weight, both as regards sign and magnitude; thus, the question had not been settled.

Up to the present I have only been able to arrange two new experiments, in which iodine and sodium hydrosulphite (in excess) were allowed to react with one another according to the equation $2\text{I} + \text{NaHSO}_3 + \text{H}_2\text{O} = 2\text{HI} + \text{NaHSO}_4$. In the old experiments iodine and neutral sulphite in the proportion $2\text{I} : \text{Na}_2\text{SO}_3$ were used. All the observations are given in Table VIII. In Experiments 5 and 6 it was not possible to examine apparatus B for alteration in weight, owing to accidents. Of the six experiments, four (Nos. 2, 3, 5, 6) gave a result not exceeding the experimental error, and thus it seems that in this reaction, generally speaking, no appreciable alteration of weight occurs. But it is noticeable that in three cases the alteration was a decrease. As regards Experiments 1 and 4, probably some disturbing influence had come into play.

Sixth Reaction : Uranyl Nitrate and Potassium Hydroxide.
 $2\text{UO}_2(\text{NO}_3)_2 + 6\text{KOH} = \text{K}_2\text{U}_2\text{O}_7 + 4\text{KNO}_3 + 3\text{H}_2\text{O}$.

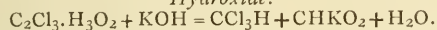
The experiment was undertaken to see whether when an element of high atomic weight was used a more pronounced alteration of weight would appear. In one limb of the Π -tubes a solution of 63.7 grms. $\text{UO}_2(\text{NO}_3)_2 + 6\text{H}_2\text{O}$ (= 50 grms. anhydrous salt) in 96.3 grms. of water was placed, and in the other 25 grms. of caustic alkali (21.35 grms. stoichiometrically necessary), and 135 grms. of water. The result was as follows:—

Date of Experiment : May, 1905.
 Kind of Vessel : Π Jena Apparatus Glass.

	No. 1. Apparatus A.	No. 2. Apparatus B.
Potassium uranate precipitated (grms.)	42.28	42.28
Observed alteration in weight (m.grm.)	+0.006	+0.002
Error in weighing (m.grm.)	± 0.009	± 0.010

Thus the weight was perfectly constant. It is to be noted that a very slight development of heat occurred.

Seventh Reaction : Chloral Hydrate and Potassium Hydroxide.



The experiment, already described in the first paper and mentioned here only for completeness sake, had led to the result $+0.012 \pm 0.024$ m.grm. when 150 grms. of chloral hydrate were converted into 108 grms. of chloroform, and thus no alteration occurred.

Eighth Reaction : Electrolysis of an Aqueous Solution of Cadmium Iodide by an Alternating Current.

The experiment, suggested by my colleague Prof. Nernst, was to show whether, when an element was repeatedly converted from the ordinary condition to a state of ionisation, an alteration of weight could be detected.

The electrolytic apparatus used consisted of a blown glass cylinder, of height 12 c.m. and diameter 4 c.m., closed at the bottom and drawn out to a point at the top. In the interior there were arranged concentrically two circularly bent platinum-foils 9 c.m. high and 2.5 c.m. in diameter, from which platinum wires led outwards through the glass wall. The two surfaces of the electrodes, which were turned towards one another, had areas of 99 and 71 sq. c.m. respectively. Two exactly similar pieces of apparatus were prepared, and one was filled with a concentrated solution of cadmium iodide, containing 40 grms. of salt in 100 c.c. A small quantity of free iodine was purposely added to the solution. When the weight and external volume of the two vessels were compared the following small differences were observed:—

	Weight (grms.)	Volume (c.c.).
Apparatus A . . .	380.158	236.718
„ B . . .	380.155	236.702
Difference . . .	0.003	0.016

For the purpose of weighing, the vessels were placed in two equally heavy (86.650 grms.) stands of polished brass, which increased the load on the scale-pan to 466.8 grms.

To produce the current a bipolar direct current motor was used, two points of the coil of which were connected with two sliding rings, from which the alternating current was taken; the number of revolutions was about 1500 per minute. The current intensity was always reduced to 3 ampères.

The process which occurs when the alternating current acts upon a solution of cadmium iodide containing some free iodine is as follows:—The cadmium remains in the liquid as a complex iodide, while a part of the iodine at the two electrodes alternately passes from the ionised condition to the metalloidal and conversely. Possibly a considerable shock to the iodine atom is thus caused. As

a current of 1 ampère in one hour separates 4.025 grm. Ag = 4.731 grms. I, when 3 ampères had acted for forty hours, which were the proportions used in the following experiments, the process must have extended to 567.7 grms. of iodine.

In the first experiments, Apparatus B, when exposed to the alternating current for forty hours, showed a decrease of weight of 0.069 m.grm., and after another forty hours a further decrease of 0.027 m.grm. There was a suspicion, however, that these alterations might be caused by a decrease in the water-film on the outer surface of the vessel, since during the electrolysis the temperature rose to about 30° or 35°. The two vessels were not treated with dilute sulphuric acid after they had been prepared, as was done with the other apparatus, and thus the film might be considerable. The vessels were then laid for a week in 12 per cent sulphuric acid, then for some days in dilute aqueous ammonia, and finally allowed to stand for a longer time under a bell-glass with calcium chloride.

The difference of weight (A - B) of the two vessels had the following values, which are the mean of four separate weighings, after A had been exposed to the action of the alternating current (3 ampères) for forty hours (first for thirty hours, then, after an interruption lasting fourteen hours, for another ten hours).

Date of Experiment : January, 1906.

	A - B.	Mean error in weighing
Before the electrolysis . .	3.145	± 0.004 m.grm.
After the electrolysis . .	3.141	± 0.005 „
Alteration . . .	0.004	± 0.009 „

Thus the alternating current analysis produced no alteration of weight, for the difference 0.004 m.grm. which was obtained, is so small that it falls within the error in weighing. The discussion of this result follows in the last paragraph of the paper.

III. Solution Processes.

Heydweiller found in his experiments that on merely dissolving copper vitriol in water a decrease of weight occurred, especially if small quantities of sulphuric acid were added. The observations in question were given in the earlier table (see Introduction), and from it we see that in five cases decreases amounting to 0.029 to 0.126 m.grm. occurred, and only in one case an increase lying within the limits of error.

My experiments extended to the solution of ammonium chloride, potassium bromide, and uranyl nitrate, when the proportions by weight of salt and water were so adjusted that at the ordinary temperature complete solution of the former resulted. The results, which do not agree well amongst themselves are collected in Table IX. (In this table is also included an old experiment with chloral hydrate, which was described in my first article).

The nine experiments with ammonium chloride show that the solution of this salt is accompanied by no change of weight. Both decreases and increases appeared, which in seven cases exceeded the limit of error of 0.03 m.grm. The increases which were repeatedly obtained, especially the considerable one of Experiment 5, might be caused by the fact that a considerable reinforcement of the water film on the outer glass surface occurred owing to the cooling which the vessel suffered during the process of solution, and perhaps it did not always return to its original state.

The alteration of weight with potassium bromide exceeds the limit of error only very slightly, and with uranyl nitrate and chloral hydrate the weight is perfectly constant.

Copper Sulphate Solution and Alcohol.

As a supplement to the above experiments I examined the case in which the ions of a salt disappear from the solution. In one limb of the Π -tubes 116.5 grms. of absolute alcohol, and in the other 107.8 grms. of copper sul-

TABLE VI.

No.	Iron and copper sulphate solution.	Date of experiment.	Copper separated. Grms.	Reaction in vessel	Observed alteration of weight. M.grm.	Error in weighing. M.grm.
1.	Without addition of alkali..	Oct.-Nov., 1902 ..	17'0	A	-0'004	± 0'006
2.	" " "	" " "	17'0	B	-0'022	0'007
3.	With addition of alkali ..	Feb.-March, 1904 .	17'0	A	-0'024	0'008
4.	" " "	" " "	17'0	B	-0'041	0'009

TABLE VII.

No.	Date of experiment.	Kind of vessel.	Iodine separated. Grms.	Apparatus.	Observed alteration of weight. M.grm.	Error in weighing. M.grm.
1.	Jan., Feb., March, 1890	η-tubes, large, old Thuringian glass..	64'9	A	-0'047	± 0'022
2.	" " " "	" " "	64'9	B	-0'114	0'013
3.	Feb.-March, 1891 . .	" " "	80'0	A	-0'103	0'022
4.	" " " "	" " "	80'0	B	-0'102	0'016
5.	May-June, 1891	" " "	160'0	A	-0'177	0'012
6.	" " " "	" " "	160'0	B	-0'011	0'013
7.	Oct., 1901	η-tubes, small, Jena apparatus glass .	43'3	A	-0'120	0'009
8.	" " " "	" " "	43'3	B	-0'098	0'009
9.	Jan.-Feb., 1904 .. .	" " "	64'9	A	-0'004	0'005
10.	Oct., 1904	η Quartz glass, closed with resin ..	64'9	A	-0'019	0'004
11.	" " " "	" " "	64'9	B	-0'033	0'014
12.	Dec., 1905	η-tubes, small, Jena apparatus glass..	54'0	A	-0'083	0'019
13.	" " " "	" " "	54'0	B	-0'053	0'020

Nos. 1—6, old experiments; 7—13, new experiments.

TABLE VIII.

No.	Date of experiment.	Kind of vessel.	Iodine used up. Grms.	Vessel.	Observed alteration in weight. M.grm.	Error in weighing. M.grm.
1.	July-August, 1890 ..	η-tubes, old Thuringian glass..	90	A	+0'105	± 0'008
2.	" " " "	" " "	90	B	-0'031	0'017
3.	Aug.-Dec., 1891 ..	" " "	110	A	+0'002	0'020
4.	" " " "	" " "	110	B	-0'127	0'017
5.	Oct.-Nov., 1901 ..	η Jena apparatus glass	50	A	-0'021	0'008
6.	Feb.-March, 1902 ..	" " " "	80	A	-0'034	0'009

Nos. 1—4, old experiments; 5 and 6, new experiments.

TABLE IX.

No.	Date of experiment.	Kind of vessel.	Quantities.		Salt in solution. Per cent.	Vessel.	Observed alteration of weight. M.grm.	Error in weighing. M.grm.
			Salt. Grms.	Water. Grms.				
Ammonium Chloride.								
1.	Nov., 1902	η-tubes, old Thuringian glass ..	37'5	150'0	20	A	-0'024	± 0'019
2.	" " " "	" " "	37'5	150'0	20	B	-0'002	0'006
3.	May-June, 1902..	O-vessels, with vacuum envelope	23'7	131'6	15'25	A	+0'008	0'006
4.	" " " "	" " "	23'7	131'6	15'25	B	+0'005	0'009
5.	June, 1902	η Jena apparatus glass	44'0	115'4	27'6	A	+0'078 ?	0'009
6.	" " " "	" " " "	44'0	115'4	27'6	B	+0'017	0'010
7.	June-July, 1903..	η Quartz vessels closed with resin	60'0	160'0	27'3	A	-0'008	0'008
8.	" " " "	" " "	60'0	160'0	27'3	B	+0'019	0'014
9.	Nov., 1903	" " "	51'0	134'0	27'6	B	-0'033	0'010
Potassium Bromide.								
1.	Feb., 1902	η Jena apparatus glass	72'5	145'0	33'3	A	-0'038	0'007
Uranyl Nitrate + 6 aq.								
1.	June, 1905	η Jena apparatus glass	136'0	136'0	50'0	A	+0'009	0'014
2.	" " " "	" " " "	136'0	136'0	50'0	B	-0'010	0'013
3.	July, 1905	" " " "	136'0	136'0	50'0	B	-0'004	0'017
Chloral Hydrate.								
1.	April, 1891	η Thuringian glass	312'0	104'0	75'0	A	-0'003	0'013

mental error of 0.03 m.grm. or even less than this error, in the reactions between—

1. Iron and copper sulphate: -0.004 to -0.041 m.grm.
2. Gold chloride and ferrous chloride: -0.009 m.grm.
3. Iodine and sodium sulphite: -0.021 and -0.034 m.grm. in the two new experiments, while the four old experiments gave + and - results.
4. Uranyl nitrate and potassium hydroxide: $+0.006$ and $+0.002$ m.grm.
5. Chloral hydrate and potassium hydroxide: $+0.012$ m.grm.
6. Ammonium chloride and water: -0.002 to 0.033 m.grm., and $+0.005$ to $+0.019$ m.grm.
7. Potassium bromide and water: -0.038 m.grm.
8. Uranyl nitrate and water: -0.004 , -0.010 , and $+0.009$ m.grm.
9. Chloral hydrate and water: -0.003 m.grm.
10. Copper sulphate solution and alcohol: -0.017 and $+0.016$ m.grm.

Heydweiller had obtained—

- (a) Large decreases of weight—
 1. In the reaction between iron and acid or alkaline copper sulphate solution: -0.097 to -0.217 m.grm.
 2. On dissolving copper vitriol in water containing sulphuric acid: -0.072 to -0.126 m.grm.
 3. On mixing copper sulphate solution and caustic potash: -0.045 to -0.092 m.grm.
- (b) Small decreases, lying within the limits of experimental error of 0.04 m.grm.—
 1. On neutralising acetic acid with ammonia: -0.026 and -0.034 m.grm.
 2. In the reaction between barium chloride and sulphuric acid: -0.016 m.grm.
 3. If an increase of weight occurred during a reaction, it was always smaller ($+0.002$ to $+0.019$ m.grm.), and lay within the limits of experimental error (0.03 m.grm.). Hence a decrease of weight is the normal phenomenon, and in those cases in which it was only small we cannot with any certainty draw the conclusion that the weight has remained quite constant.
 4. No connection has been found between the alteration of weight and the appearance or disappearance of electrons. (See the experiments given in Section III.).
 5. There now occurs the question how the decreases of weight are to be explained. It might be suspected that they were due to an external cause, which has not yet been discovered, but taking into account the care with which all the possibilities were investigated, this view seems to be improbable. On the other hand, the fact that the alteration occurs to a marked extent only with certain reactions, such as the reduction of silver or iodine, and is either small or does not occur at all in others, clearly points to a connection with the chemical process.

As the explanation must be of such a nature that it accounts only for decreases and never leads us to expect increases, no other hypothesis seems to remain open, except that already mentioned in the introduction, according to which the phenomenon is due to the releasing of small particles from the chemical atoms. In the case of the radio-active elements, Rutherford and Soddy's hypothesis, which has been thoroughly established, assumes that the cause of the changes they undergo depends upon a gradual disintegration of the atom, which, however, extends only to a small fraction of the total mass, and occurs spontaneously. When chemical reactions take place between two substances, the theory that in consequence of the great shock which the atoms suffer, a small part of their mass splits off, does not seem impossible, especially in view of the considerable decrease of the potential atomic energy which occurs during changes which take place of themselves and with great development of heat. Whether, then, a more complete disintegration of a

few atoms occurs, as with radio-active substances, or whether all the atoms concerned suffer a slight loss, remains undecided. But even in the latter case it would be conceivable that the atoms attacked still retain in essentials their original properties, since they experience only a very small alteration of their composition. Finally, the nature of the released fragments must be left undecided. Electrons do not seem to become free during chemical reactions, at least Martinielli (*Atti R. Acad. dei Lincei*, 1904, [5], xiii., II., 217; *Chem. Centralbl.* 1904, ii., 1096) found that on dissolving copper sulphate in water containing sulphuric acid, or potassium bichromate in water, or on the reduction of silver phosphate with ferrous sulphate, no ionisation of the air surrounding the substances occurred. M. R. Campbell observed the same (*Phil. Mag.*, 1905, [6], ix., 545; *König's, Beibl.*, 1905, 1070).

The theory of the partial disintegration of the atom does not agree with the observation that when a cadmium iodide solution is electrolysed by means of an alternating current, no decrease of weight takes place, although the process of alternately binding and separating off electrons from the iodine atom has extended to about 568 grms. of iodine. Yet it is conceivable that this reaction, although it is connected with a considerable change of the properties of an element, yet causes no such great shock to the iodine atom as the reaction between iodic acid and hydriodic acid, when in the first substance three atoms of oxygen and one of hydrogen, and in the second one atom of hydrogen, are torn from the iodine. Moreover, it is perhaps possible that during the experiment the change of current occurred too rapidly in proportion to the duration of the reaction; a repetition of the experiment with a direct current commuted at suitable intervals would decide this.

Finally, there is the following point to be considered:—The decreases of weight during the reactions will be explicable only if we assume that a part of the mass passes out through the glass wall. The possibility of this is difficult to estimate on account of our ignorance of the particles passing through, but it may be supposed that their magnitude, as they are fragments of an atom, is much less than that of an ordinary molecule. Yet it must be remembered that carbon dioxide slowly passes through glass (Bunsen, *Wied. Ann.*, 1883, xx., 558), and moreover, that the latter, though certainly not until temperatures of about 600° and upwards, is penetrable by hydrogen and by air to a considerable extent (Berthelot, *Comptes Rendus*, 1905, cxl., 817, 821, 1253, and others), just as glowing quartz walls are penetrated by helium (Jaquero and Perrot, *Comptes Rendus*, 1904, cxxxix., 789). Moreover, helium, even of the ordinary temperature, seems to penetrate into glass, and to very different degrees (Ramsay and Soddy, *Zeit. Phys. Chem.*, xlviii., 693). On the other hand, glass tubes of diameter 8 m.m. and 1.5 m.m. thickness of wall have been found to be absolutely impermeable towards hydrogen at 40 to 126 atmospheric pressure (Quincke, *Pogg. Ann.*, 1877, clx., 118). If any penetration occurs, the quality of the glass wall must undoubtedly exercise an influence. This is shown by the fact that during the reaction between silver salts and ferrous sulphate there was hardly any decrease of weight when the inner side of the vessel was made impermeable by covering it with a layer of paraffin (Expts. 7, 8, and 12, 13). The thickness of the walls, as well as the composition of the glass, must be taken into account, and special experiments must be performed, in which one and the same reaction will be tested in glass vessels of very different quality. The non-agreement of the results which appeared when the reactions (e.g., iron and copper sulphate) were examined by different workers, is perhaps due to the difference of the glass vessels.

For the present I am obliged to break off the experiments and to publish the results I have so far obtained in this incomplete form. In the future I hope to be able to continue the research at the Physikalisch-Technischen Reichsanstalt, which has kindly offered me suitable accommodation.

THE ATOMIC WEIGHT OF RADIIUM AND THE PERIODIC SYSTEM.

By HARRY C. JONES.

THE question of the atomic weight of radium cannot be regarded, as yet, as settled. We have, on the one hand, the determination, by purely chemical means, made by M^{de}me. Curie, which gave the value 225 (*Ann. Chim. Phys.*, 1904, [7], xxx., 137). On the other, we have the work of Runge and Precht (*Phil. Mag.*, 1903, [6], v., 476), based on a physical method, which gave a much higher value—258.

It is difficult, at present, to decide between these two. The value based upon spectrum analysis (258) places radium in the periodic system *after* thorium and uranium. In terms of the relation between the mass of the atom and its radio-activity, this is the position which it should occupy. The greater the mass of the atom, the less its stability, and, consequently, the greater its radio-activity.

Various lines of argument have been advanced in favour of the value 225. Perhaps the most important of these is the argument based upon the position of radium in the periodic system. Radium is closely allied chemically to barium, and the value 225 for its atomic weight places it in the same group with barium in *series twelve*.

This line of argument has had considerable weight, and has been used in favour of the smaller mass for the atom of radium.

The object of this paper is to point out that if the atomic weight of radium is slightly greater than 250, it would find a place in the periodic system quite in accord with all its chemical and physical properties. Indeed, the position which it would then occupy would be rather more satisfactory than that which it would take if its atomic weight were 225.

If the atomic weight of radium were 252 to 256 it would fall in Group II. of the periodic system, along with barium and its homologues, but in a new series—*series thirteen*.

That this is the case can be seen by a glance at Mendeleeff's table of the periodic system. If we compare the atomic weights of the elements in a given group and in any two succeeding series, we shall find for the elements with the higher atomic weights a difference in the atomic weights, in general, of from 25 to about 31 or 32 units.

Thus, the atomic weight of strontium is 87.6, that of cadmium 112.4—difference 24.8. The atomic weight of barium is 137.4, which differs from that of cadmium by 25 units.

Passing to Group III., the atomic weight of yttrium = 89 differs from that of indium = 115 by 26 units. Indium differs from lanthanum = 138.9 by 23.9 units, lanthanum differs from ytterbium = 173 by 34.1, and ytterbium differs from thallium = 204.1 by 31.1 units.

Turning to Group IV., similar relations manifest themselves. Zirconium, atomic weight 90.6, differs from tin, whose atomic weight is 119.0 by 28.4 units. Tin differs from cerium, whose atomic weight is 140.25, by 21.25 units. Cerium differs from lead, whose atomic weight is 206.9, by 66.65, but since cerium is in Series 9 and lead is in Series 11, and there is no member in this group in Series 10, we must divide the above difference by 2, which gives us a difference per series of 33.32. Lead differs from thorium, whose atomic weight is 232.5, by 25.6 units.

In Group V. the following differences appear:—Vanadium, with an atomic weight of 51.2, differs from arsenic, with an atomic weight of 75, by 23.8. Arsenic differs from niobium = 94 by 19 units. Niobium from antimony = 120.2 by 26.2 points. Antimony from tantalum = 183 by 62.8, but since one series is missing between these two, this difference must be halved = 31.4. Tantalum differs from bismuth = 208.5 by 25.5.

In Group VI. relations of the same kind appear. Chromium, whose atomic weight is 52.1, differs from selenium = 79.2 by 27.1 units. Selenium differs from

molybdenum = 96 by 16.8 units. Molybdenum differs from tellurium = 127.6 by 31.6 points. Tellurium differs from tungsten = 184.0 by 56.4, but as one series is here missing this must be halved = 28.2. Tungsten differs from uranium = 238.5 by 54.5, and halving this, on account of the missing series, we have 27.2.

The above relations suffice to show that two successive members in any group of the periodic system usually differ, in their atomic weights, by a number that is close to from 25 to 28, and may reach 31 or 32, or even higher. This shows that an atomic weight slightly greater than 255, and which might be as high as 257 or 258, would place radium quite as satisfactorily in the periodic system as the lower value 225.

It might be objected that there is no other member of Series 13 known, and that it would be *creating a new series* just for one element—radium.

It is difficult to see the force of this argument in the light of the facts. In the first place, we know, at present, only two members of Series 12—thorium and uranium. Both of these are radio-active, but only feebly so.

While the placing of radium in Group II., Series 12, brings it in the same group with its chemical relative barium, it at the same time places it in a position which is not in keeping with its most characteristic physical properties. Think of radium as compared with thorium and uranium, or with any other chemical element. It is at least 1,500,000 times as radio-active as uranium. It has the property of charging itself electrically, of lighting itself, and of giving off enormous quantities of heat energy. It is the only element known that has any of these properties to a determinable degree.

Further, it is very unstable, breaking down spontaneously and yielding another chemical element—helium—as one of its decomposition-products.

When we think of these properties alone it seems much more natural to place radium in a series by itself, following the series containing the slightly radio-active elements—thorium and uranium—than to place it in a series with any other chemical element or elements.

If we examine the evidence existing in favour of the value 225 we find, in the first place, the direct determination by M^{de}me. Curie. It must be admitted that this is far from satisfactory, for a number of reasons. The small quantity of material at disposal made the result less accurate, assuming that the material was pure. A number of the operations to which it was subjected, such as removal of the water by heating in the air, are open to criticism.

Another argument in favour of the 225 value is based upon the fact, now pretty clearly established, that radium is a decomposition-product of uranium, and must have a smaller atomic mass than the substance which produced it. This line of argument has been invalidated by the observation that *radium is certainly not formed directly from uranium*, but intermediate substances are produced, and, as Joly has pointed out (*Nature*, 1904, lxx., 80), the radium probably results from the interaction of these products with some of the elements in pitchblende. Its atom could then easily have a mass greater than the atom of uranium itself, since radium would thus be a product of synthesis and not of decomposition. It must be stated that certain determinations by Watts (*Phil. Mag.*, July, 1903, [6], vi.) and others, using relations between the spectral lines, led also to a value close to 225. The meaning of this remains to be explained.

The direct argument in favour of the higher value is furnished by the beautiful investigation of Runge and Precht. By means of certain relations between the spectral lines and the atomic weights of the elements producing them, which have been shown to hold for the members of a given group, as the magnesium, calcium, strontium, barium group, they were led to an atomic weight for radium of 257.8, or in round numbers 258.

As shown above, this would not move radium "two rows further down in the column Mg, Ca, Sr, Ba," as stated by Runge and Precht, and to which objection must be

offered, but *only one row*, making it the only member of Series 13.

The atomic weight of radium can be settled, finally, only after a considerable amount of pure material is available. As some time must elapse before this is realised, the best we can do at present is to take the evidence available. The object of the present note, as has been stated, is to call attention to the fact that the argument based upon the periodic system, in favour of 225 as the atomic weight of radium, is not well founded. Indeed, the evidence from the periodic system is certainly as strong, and in the opinion of the writer much stronger, in favour of a higher value, which would be very nearly that found by Runge and Precht.—*American Chemical Journal*, xxxiv., No. 4.

PERKIN MEMORIAL AND INTERNATIONAL JUBILEE OF THE COAL-TAR COLOUR INDUSTRY.

THE year 1906 marks the Fiftieth Anniversary of the epoch-making discovery by William Henry Perkin of the dyestuff "Mauve" by which the foundation was laid of the coal-tar colour industry, and a great stimulus given to the study of organic chemistry.

The discovery, which was destined to have such far-reaching consequences, was made in the Easter vacation of 1856, whilst Perkin, then only a lad of eighteen, was working in a private laboratory he had fitted up in his father's house. The colouring matter was patented on August 26th of the same year, and in the early part of the following year the erection of the first coal-tar colour works was commenced at Greenford Green, near Harrow. Here mauve was soon produced in quantity, and here were manufactured later other coal-tar dyestuffs, including artificial alizarin. From these small beginnings the industry has now grown to dimensions which neither the discoverer nor any man of his time could have foreseen. Not only has an enormous and highly scientific industry been established, the value of which with its collateral branches has been estimated at over twenty million pounds per annum, but the dyeing and textile industries, important and flourishing trades in this country, have been subjected to a complete revolution by which they are being emancipated from their former rule-of-thumb methods and changed from empirical arts to branches of applied science. A profound influence has also been exerted upon the entire chemical trade of the world, and several daughter industries, such as the manufacture of synthetical medicinal agents, antiseptics, synthetic perfumes, artificial sweetening materials, &c., have been called into existence. Side by side and closely interrelated with this great technical progress is the immense stimulus which the establishment and rapid growth of the coal-tar industry has given to the study of pure organic chemistry, especially that of ring carbon compounds.

The discoverer, Dr. Perkin, being fortunately still with us in full activity, it has been widely felt both in this country and abroad that a fitting celebration of the jubilee of the industry should be held which should be made the occasion of a public tribute to its founder in recognition of his great services to chemical industry and chemical science.

At a public meeting held at the the Mansion House, on February 26th, under the chairmanship of the Lord Mayor, the following resolutions were unanimously adopted:—

- I. That in view of this being the Fiftieth Anniversary of the foundation of the coal-tar colour industry, it is desirable that steps should be taken to commemorate the event, and to do honour to W. H. Perkin, the founder.
- II. That an appeal be made in this country and abroad for subscriptions for carrying out the following objects:—

1. The presentation to Dr. Perkin for his lifetime of an oil portrait of himself executed by an eminent artist, the portrait to become the property of the nation at his death.
2. The execution of a marble bust of Dr. Perkin to be placed in the rooms of the Chemical Society.
3. The establishment of a "Perkin Research Fund" for the promotion of chemical research, to be administered through the Chemical Society.

In carrying out these recommendations the hearty support has been secured of the entire scientific world, and a strong international committee has been formed comprising the most prominent men of science and industry in this and other countries.

The subscriptions already received amount to over £2000.

In inviting co-operation it is pointed out that donations may be allocated specifically, if desired, to any one of the above mentioned objects.

The following is the complete programme which has been arranged for the Jubilee Celebration to take place in London on July 26th and 27th:—

July 26th.—

11.0 a.m. Meeting at the Royal Institution for the Presentation to Dr. Perkin of Portrait, Bust, Addresses, &c. Ladies are invited.

7.0 p.m. Banquet at the Whitehall Rooms, Hotel Metropole. Many distinguished guests are expected to be present.

July 27th.—

2.0—6.0 p.m. Visit to the original Works at Greenford Green where Mauve was first manufactured, and Garden Party at Dr. Perkin's house. Train from Paddington (G.W.Ry.) at 2.15 p.m. to Greenford. Return from Sudbury by G.C.Ry. at 6.0 p.m. Ladies are invited.

8.30 p.m. Soirée at the Leathersellers' Hall, at the invitation of Dr. and Mrs. Perkin. Ladies are invited.

Institute of Chemistry.—An examination in Biological Chemistry will be held at the Laboratories of the Institute on Tuesday, October 23rd, 1906, and three following days. This examination is open to any Fellow or Associate of the Institute, to any Candidate whose application for admission to the Final Examination has been accepted by the Council, and to any Candidate who has passed the Intermediate Examination of the Institute. The Examination extends over at least four days, and may be theoretical, practical, written, and oral. The syllabus includes Biological Chemistry, with special reference to Fermentation, Enzyme-action, the Chemistry and Bacteriology of Food-stuffs, Water Supply, and Sewage Disposal, and to the application of Biological Chemistry to Industries and manufactures. Candidates intending to enter for this Examination are recommended to study the following subjects:—1. Elementary Biology. 2. The Morphology, Physiology, and Life History of Bacteria, Yeasts, and Moulds, in their relation to Food, Water Supply, the Treatment of Sewage, Agriculture, and the Fermentation Industries. (A special study of pathogenic organisms is not demanded, but the Candidate should acquire a knowledge of such as are of importance in relation to Food and to Water Supply). Practical work should include:—(a) General bacteriological methods and preparation of pure cultures; (b) Microscopy, the staining and mounting of preparations, and the recognition of species; (c) Fermentation changes caused by micro-organisms. 3. Enzymes and their actions. 4. The methods employed in the examination and estimation of the carbohydrates. 5. The proteids and their decomposition products.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

CONVERSAZIONE AT BURLINGTON HOUSE.

THE second, the Ladies' Soirée, took place on June 20th. Among the more important exhibits were the following :—

Sir JAMES DEWAR, F.R.S.

1. New Charcoal Calorimeter and Thermoscope.—Charcoal at the temperature of liquid hydrogen that has absorbed at atmospheric pressure considerable quantities of helium or hydrogen—or alternatively of nitrogen, oxygen, or air at their respective boiling points—is utilised in this instrument as a material that, by reason of changes in the volume of the occluded gas, exhibits great sensibility to heat and light radiation, and can be used in calorimetry at the temperature of solid hydrogen.

2. Charcoal Vacua.—Electric Discharge Tubes showing gradual gas absorption by charcoal cooled in liquid air until, after the Röntgen radiation stage, the electric resistance becomes so great that a discharge will not pass.

3. Spectrum Tubes.—(1). The less condensable gases of the atmosphere—Helium and Neon. (2). The more condensable gases of the atmosphere—Krypton and Xenon. Each set of gases being separated by the charcoal method.

4. Some Scientific Uses of Liquid Air.—(1). Electric ice crystals. (2). Rough measures of relative thermal conductivities in metals and alloys, by observing the height of the deposited ice cap when similar wires are placed along side each other and the ends immersed in liquid air. The relative conductivities are as the squares of the height of the ice columns. (3). Spheroidal state of liquid air on the surface of different fluids and solutions, showing changes of volatility from the varying amount of vapour condensation; at the same time exhibiting interesting rotatory and translatory movements.

Mr. OLIVER S. DAWSON.—Photographic Prints in Natural Colours (Smith-Merckens process).

The specimens of prints shown have been made in an ordinary printing frame, by one exposure to light, and when taken out of the frame possess the colours which they exhibit. Ordinary "printing-out" paper is only capable of recording black and white, and the intermediate shades of grey. This "printing-out" paper records every colour and shade. It necessitates using in the printing frame, instead of the ordinary negative, a coloured positive. The cost of colouring a positive from an ordinary negative is small.

ORDNANCE COLLEGE, WOOLWICH.—Microphotographs of Brass, &c.

Two of the photos are of the same place on the piece of metal. One of them has been simply rotated on its axis through a few degrees. The same side illumination in each case. The dark structures in the one show as light ones in the other.

Mr. J. E. STEAD, F.R.S.—A Triple Alloy of Tin—Antimony—Arsenic, polished and etched, showing bright curved crystals embedded in a soft matrix or eutectic. (See p. 231).

Mr. KENNETH J. TARRANT.—Photographs of Electrical Discharges, at atmospheric pressure and in vacuo.

A series of photographs showing the characteristic discharge from an interrupted continuous current and a high frequency oscillating one, also between parallel conductors both insulated and bare, of varying capacity, and with various condenser conditions. Also the apparently spiral (vortex) nature of the discharge both in air and in vacuo.

Mr. R. G. DURRANT.—Evidence to show that Ionic Separation occurs when Solutions of Acids or of Salts are allowed to Diffuse into Sensitised Jellies or Solutions.

Tubes, diagrams, and experiments to illustrate that—(1). Acids when they diffuse into blue litmus jellies produce a purple zone in advance of the diffusion-front and (where the acid has a bleaching anion) a yellow-red zone behind the diffusion-front. (2). An acid mixed with litmus, on diffusing, leaves the litmus behind. (3). Hydrogen occluded by palladium would appear to be partially acidic. (4). When concentrated silver nitrate solution diffuses into purple litmus under suitable circumstances, red, blue, colourless and grey-blue—corresponding to H, OH, NO₃, and Ag appear in this order. At certain periods sharp bands may form whose boundaries, if measured from the diffusion start, almost exactly correspond to the known mobilities of these ions.

Messrs. CARL ZEISS, Jena.—Photomicrographic Apparatus for Ultra-violet Light. (Designed by Dr. A. Köhler).

The apparatus consists of a table-top with spark stand, collimator, prism of quartz (which separates rays of different wave-lengths proceeding from the source of light), a collector (which combines the rays of each wave-length into a spark image), a vertical camera with time shutter, microscope with sole-plate; the whole on a second table-top. The camera is mounted on a graduated rod so arranged that it can be swung aside, a special searcher with carrier is provided to be interchanged with camera. The objectives are monochromats specially computed by Dr. M. von Rohr, member of the scientific staff of Messrs. Carl Zeiss, Jena. The objectives are made of fused quartz corrected for $\lambda = 275 \mu$, and 160 m.m. tube length. The highest power is of 1.25 N.A., which when working with ultra-violet light is equal in resolving power to an ideal objective of 2.50 N.A. when white light is used. The lenses of eyepieces and condenser are made of quartz. The rays of the required wave-length on emerging from the collector fall upon a reflecting prism underneath the stand which directs them into the microscope. The image is projected upon a fluorescent screen in the searcher and examined by means of a powerful magnifier. The searcher is so constructed that when the camera is turned in its place the image will appear sharp on the ground-glass screen when a camera extension of about 30 c.m. is used. The source of light is supplied by a current of sparks of Leyden jars charged by an induction coil for greater convenience. Photographs of diatoms taken with this apparatus are shown on the table.

Dr. O. SILBERRAD and Dr. R. C. FARMER.—Stability Test for Cordite.

Illustrating a method recently devised at the Chemical Research Department, Royal Arsenal, Woolwich, for the determination of the stability of cordite and other propellant explosives. It is well known that these explosives decompose gradually on storage, and may eventually ignite spontaneously, if their stability be not tested from time to time. The principle of the new test is based upon the results of several thousand experiments, and is the only method known which gives reliable results with cordite. The test has been adopted by the Service, and will shortly be made use of as a safeguard against spontaneous explosions in powder magazines, particularly in the tropics, where the deterioration takes place most rapidly. In examining cordites the procedure is briefly as follows:—50 grms. of the explosive are maintained at 70°C. in a glass vessel fitted with a mercury manometer: the alteration in pressure is measured at intervals. A contraction takes place at first owing to the absorption of oxygen from the air; subsequently a gradual expansion occurs, the former of these phenomena has never previously been observed.

Sir WILLIAM CROOKES, F.R.S.

1. Stereoscopic Photographs, taken by Sir W. Crookes on the occasion of the visit of the British Association to South Africa in the autumn of 1905.

2. Occurrence of the Diamond.—"Blue Ground" in which diamonds are found; from the 2120 ft. Level, De Beers Mine. Diamantiferous gravel from the Pulsator, De Beers Mine. Selected stones from the Pulsator, De

Beers Mine. Cut and polished section of a piece of silicified wood, found by Mr. Jesse Browne about twelve years ago in the untouched "Blue Ground" of the Du Toits Pan Diamond Mine, Kimberley; the wood bears a great resemblance to the wood of the Camel-Tree (*Acacia Giraffa*) of South Africa. Polished section of the Canyon el Diablo Meteorite, in which diamonds have been found.

Models of Crystals of Diamond.—(1). Diamond in the form of a hexakisoctahedron (the forty-eight scalenohedron), or a solid figure contained by forty-eight scalene triangles. According to Professor Maskelyne this occurs as a self-existent form only in the diamond. (2). Diamond in the form of a hexakisoctahedron and octahedron; from Sudafrika. (3). Diamond in the form of octahedron with intersections. (4). Diamond from Brazil. (5). Diamond from Sudafrika. (6). Diamond from Brazil. (7). A macle or twin crystal, showing its formation from an octahedron with curved edges.

Mr. G. F. HERBERT SMITH.—Precious Stones and Simple Methods for their Identification.

This exhibit illustrates the variety of precious stones available for ornamental purposes. A gem stone must be hard enough to resist the abrasive action of ordinary dust, and at the same time be either transparent or, if opaque, of pleasing colour. The number of mineral species suitable for the purpose is not so restricted as popularly supposed. The names employed by jewellers frequently differ considerably from the scientific nomenclature, being often associated with certain colours rather than particular species, e.g.—topaz (yellow), sapphire (blue), ruby (red), emerald (green), and amethyst (violet). The colour though the most obvious character of a stone is the least trustworthy; and the hardness while of immense importance as regards its durability is of little discriminative value. On the other hand, the optical characters (refractivity, double refraction, and dichroism) and the specific gravity may be easily and accurately determined, and lead to the precise identification of the stone. In the case of practically all faceted transparent stones the refractivity and double refraction are sufficient for the purpose, and the stone need not be removed from its setting. Some simple apparatus for the identification of precious stones is exhibited.

Dr. G. T. MOODY.—Specimens Illustrating the Indifference of Oxygen towards Iron in presence of Water and the Effect of the Admission of Carbonic Acid.

(1). Specimen of soft Swedish iron which has been in contact with air and water both completely freed from carbonic acid for five weeks. During this period approximately 56 litres of air passed over the iron, exposing the metal to a volume of oxygen exceeding thirty times the amount required to completely convert it into ferric oxide. (2). Specimen of the same iron which had remained perfectly bright after exposure for three weeks to water and 32 litres of air, freed from carbonic acid. At the end of the period named, air cleaned by its passage through a tower packed with moist pumice-stone, but containing its normal amount of carbonic acid, was admitted. After 72 hours, during which time approximately 16 litres of air passed through, and when considerable rusting had occurred, the tube was sealed.

Dr. F. D. CHATTAWAY.—Copper Mirrors obtained by the Deposition of Metallic Copper upon Glass.

The method of silvering glass by depositing the metal in a thin film by reduction of some soluble silver compound has long been employed in the production of mirrors, but, hitherto, no method of similarly depositing copper in a brilliant film has been discovered. The exhibit shows a number of glass vessels on which copper has been thus deposited by a slow reduction of the black oxide. The metal being protected from the air such mirrors retain their lustre permanently.

Prof. W. GOWLAND.

1. Portion of a Meteorite containing Diamonds found

near Cañon Diablo, Arizona, and specimens of Diamonds extracted from it.

2. Alloys of Copper and Calcium.—A series of alloys ranging from 0.8 to 61.5 per cent of calcium. All are brittle, and those containing 6 to 7 per cent calcium extremely hard. The higher alloys decompose water, and are readily oxidised in the air. Specimens are also exhibited showing the effects of calcium on lead, tin, bismuth, aluminium, and coinage bronze.

Mr. A. A. C. SWINTON.—Visibly Luminous Electrical Discharges in vacuo obtained with comparatively low Electrical Pressures.

Edison, Fleming, and others have shown that the passage of the electric discharge in vacuo is much facilitated by heating the cathode. Owen and Wehnelt have proved that this effect is enormously increased if the heated cathode be coated with oxides of the alkaline metals. The present experiments show that similar results can be obtained by coating the cathode with radium, and that the effect will be greater when the cathode is heated than obtains without heating.

In the Meeting Room Sir WILLIAM CROOKES gave a demonstration of Lantern Slides and Experiments in illustration of some Properties of the Diamond.

Lantern Slides.—Surface workings at Wesselson Mine. Diagrammatic section of the "Pipe." The "Pipe," Kimberley Mine. Heap of diamonds in the De Beers Sorting Office; 25,000 carats. Diamonds sorted into sizes. Large diamonds. Large crystal of diamond. Curious crystals of diamond. The Cullinan diamond. Triangular markings on diamond (natural and artificial). Glass shavings of spiral form. Radio active diamonds. Diamond from meteorite. Artificial diamond from granulated iron. Artificial diamond from explosion vessel.

Experiments.—A. Sprouting graphite. B. Natural crystal of diamond showing colours in polarised light. C. Natural crystal of diamond in which double refraction is induced by great pressure. D. Hardness of diamond illustrated by squeezing a natural crystal into steel by hydraulic pressure. E. The depolymerisation of diamond in the electric arc.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 22, May 28, 1906.

Variations in the State of Amorphous Carbon under the influence of Temperature and under the Action of Temperature Oscillations.—O. Manville.—When amorphous carbon is reduced to powder and all the occluded gases got rid of by the combined action of heat and low pressure, the author finds that, if the resulting powder is placed in a current of oxygen and the temperature slowly raised, carbon anhydride and carbon monoxide are produced, the temperature of formation depending on the nature of the carbon, on its physical and chemical state, on the velocity of the current of oxygen, and on the time.

Acid Phosphites of Primary Cyclic Amines.—P. Lemoult.—The author investigates the products of the action of PCl_3 on certain primary cyclic amines. The reactions, which seem very complex, consist in the decomposition by fixation of the elements of water, resulting in the acid phosphites of the amines in question. Hitherto these compounds have not been investigated, on account of the difficulty of their preparation by direct combination of the base with phosphorous acid. The author's preparation is, however, in practice quite simple, and results in the following compounds:—Acid phosphite of aniline, $\text{PO}_3\text{H}_3\text{C}_6\text{H}_5\text{NH}_2$;

acid phosphite of *o*-toluidine, $\text{PO}_3\text{H}_3, \text{C}_6\text{H}_4\text{CH}_2\text{NH}_2$; and
 acid phosphite of *as-m*-xylylidine, $\text{PO}_3\text{H}_3, \text{C}_6\text{H}_8\text{CH}_2\text{NH}_2$.
 In general, the action of PCl_3 on the primary cyclic amines in presence of ether or chloroform gives phosphorated products soluble in these solvents, and the hydrolysis of which produces the acid phosphites of the amines used.

Absolute Atomic Weight of Terbium.—G. D. Hinrichs.—M. Urbain's determination of the atomic weight of terbium (159.22) depends on the values $H=1.007$ and $S=32.06$ used in the calculations. The author applies his correction to the ordinary reduction to determine the absolute atomic weight of terbium. The method used is to weigh the crystalline sulphate, $\text{Tb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, and weigh it again after complete desiccation, $\text{Tb}_2(\text{SO}_4)_3$. The author applies his correction, and brings out the absolute atomic weight to be 159.07 as the mean of three experiments.

Pure Ferro-tungstens.—Em. Vigouroux.—By the aluminothermic method, wolfram-irons can be prepared in which the proportion of tungsten reaches 46.25 per cent. These pure ferro-tungstens, when exhausted by dilute hydrochloric acid, which acts upon the free iron only, leave a body in which the proportion of tungsten increases, and is finally maintained at a constant proportion of 68.70 per cent—an amount corresponding to a compound of formula Fe_3W_2 .

Hydro-anthracenic Derivatives.—Marcel Godchot.—The author prepares a series of hydro-anthracenic derivatives by hydrogenation. Octahydroanthranol, $\text{C}_6\text{H}_{10}\text{CH}_2\text{CHOH}$, results from the hydrogenation of hexahydroanthrone. Anthracenehexahydride, $\text{C}_{10}\text{H}_{16}$, is prepared from octahydroanthranol by a process of dehydration. Anthracene tetrahydride by hydrogenation of dihydro-*i*-oxanthranol by use of H_2 . γ -Dibromo-anthracene tetrahydride is prepared from the latter by the action of bromine.

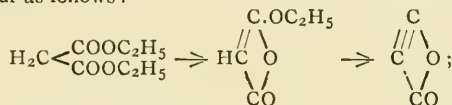
A Qualitative Reaction of Phosphorus.—M. Mauriceau-Beaupré.—The author utilises the property which vapours of phosphoric acid have of corroding fusing glass, and which property is possessed by no other acid except hydrofluoric, as a means of detecting the presence of phosphorus in qualitative reactions.

New Method of Microscopic Analysis of Flour.—G. Gastine.—To detect adulteration of flour the author devises the following method. The flour is impregnated with a colouring solution, slowly dried, and then exposed for some minutes to a temperature of 110–130° and examined under the microscope in Canada balsam, when extraneous matter can be detected with ease.

Berichte der Deutschen Chemischen Gesellschaft.
 Vol. xxxix., No. 8, 1906.

Hydrates of Chromium Chloride.—A. Werner and A. Gubser.—The following hydrates of chromium chloride are known:— $[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$, blue hexahydrate; $[(\text{OH}_2)_4\text{Cr}(\text{OH}_2)_4]\text{Cl}$, green hexahydrate; $[\text{Cl}\text{Cr}(\text{OH}_2)_4]\text{Cl}$, green tetrahydrate; and Godefroy's green decahydrate, prepared by allowing a solution of the green hexahydrate to crystallise at a low temperature. The investigation of this decahydrate showed that two of its chlorine atoms are directly bound with the chromium atom, and one indirectly. All the three green hydrates contain the residue $[\text{Cr}(\text{OH}_2)_4]$. The hydrate with four molecules of water is the normal chloride of this monovalent positive radical, while the decahydrate appears to be $[(\text{OH}_2)_4\text{Cr}(\text{OH}_2)_4]\text{Cl}$.

Constitution of Carbon Suboxide.—Arthur Michael.—The structure assumed for the substance obtained when alcohol was split off from malonic acid ester was based upon the theory that the decomposition occurred symmetrically (Diels and Wolf, *Ber.*, 1906, xxxix., 689; *CHEM. NEWS*, 1906, xciii., 141). This, however, is in contradiction to our experience of all other such decompositions which lead to the formation of ring derivatives. From analogy with the formation of dimethyl furfuran from acetonyl acetone, the decomposition of malonic acid ester might occur as follows:—



and thus the so-called sub-oxide is the lactone of β -hydroxy-propionic or propiolic acid. This composition agrees with the chemical behaviour of the substance.

MISCELLANEOUS.

Honours to British Research Laboratories.—Although scientific research receives little encouragement in this country it is gratifying to find that the labours of British scientists are recognised abroad. The Awards to the British Section of the recent Liège Exhibition were distributed at the Mansion House on June 13th, and the following presentations were made:—Wellcome Chemical Research Laboratories, one Grand Prize, one Diploma of Honour, and two Gold Medals; Wellcome Physiological Research Laboratories, one Grand Prize and two Gold Medals. Medals were also awarded to the respective directors of these institutions.

Society of Arts.—The Council of the Society of Arts have awarded the Society's Silver Medal to the following readers of papers during the Session just completed:—Mr. W. F. Mitchell, "The Commerce and Industries of Japan"; Dr. William Arthur Aikin, "Aspects of Voice Development"; Mr. Leon Gaster, A.M.I.E.E., "Progress in Electric Lighting"; Mr. Walter Garstang, M.A., "The Fisheries of the North Sea"; Captain G. S. C. Swinton, "London Traffic"; Mr. Bernard B. Redwood, B.A., "Motor Boats"; Mr. J. B. Millett, "Submarine Signalling"; Professor Thomas Oliver, M.A., M.D., LL.D., "Bridge Building by means of Caissons"; Mr. Clayton Beadle, "Watermarking"; Sir James A. Bourdillon, K.C.S.I., "The Partition of Bengal"; Dr. George A. Grierson, C.I.E., "The Languages of India"; Colonel Sir Arthur Henry McMahon, K.C.I.E., C.S.I., "Seistan"; The Hon. Rodolphe Lemieux, K.C., "French Canada"; The Hon. J. G. Jenkins, "Social Conditions in Australia"; Mr. Louis N. Parker, "Historical Pageants"; Mr. H. Yates Thompson, F.S.A., "Illuminated Manuscripts"; Mr. Harry Powell, "Cut Glass."

MEETINGS FOR THE WEEK.

MONDAY, July 2nd.—Faraday Society. (Special Meeting, to which the public are invited) "Oxidation of Atmospheric Nitrogen in Electric Arcs," by Prof. Kr. Birkeland, of Christiania. Mr. F. W. Harbord will communicate a paper written by Dr. Eugen Haanel, of Ottawa, describing the recent experiments on electric iron and steel smelting that were made at Sault Ste. Marie on behalf of the Canadian Government. (The Meeting will be held at the Society of Arts at 8 p.m.)

THURSDAY, 5th—Chemical, 8.30. "Saponarin—a New Glucoside, coloured Blue with Iodine," by G. Barger. "Constitution of Umbellulone," by F. Tutin. "Electrolytic Oxidation," by H. D. Law. "Action of Ethyl Iodide and of Propyl Iodide on the Disodium Derivative of Diacetylacetone," by A. W. Bain.

FRIDAY, 6th.—Finsbury Technical College Old Students' Association, 7. (General Meeting).

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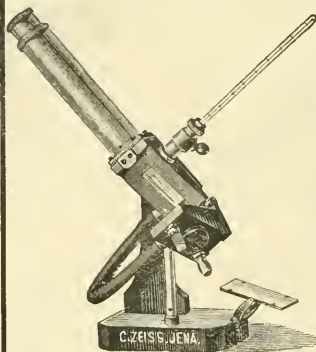
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THE CHEMICAL NEWS.

VOLUME XCIV.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2432.—JULY 6, 1906.

NOTES OF A COURSE OF LECTURES ON THE OLD AND NEW CHEMISTRY.*

I. EXTRACTS FROM DIFFERENT AUTHORS RELATING TO THE OLD CHEMISTRY.

By Prof. Sir JAMES DEWAR, F.R.S., &c.

CHEMICAL PERIODS.

I.

It extends from the earliest period to the first centuries of the present era, and may be divided into three sections.

1. The history of chemical knowledge among the nations of antiquity down to the seventh century B.C. It includes what little is known of the chemical arts of the Indians, Egyptians, Hebrews, and other nations of antiquity. We can only judge of these from their metals, glass, colours, and other antiquities.

2. From 640 B.C. down to the second or third century A.D. It includes the arts of the Greeks and Romans, both as judged from their remains and from the allusions in their literature, and especially their speculations. The latter attract us by the names of Thales, Empedocles, Democritus, Leucippus, Aristotle, Lucretius, and a host of others. This is the epoch of the subjective evolution of natural laws.

3. This section coincides with the rise and progress of mysticism in the later Alexandrian schools. It is in this period that chemistry first appears as a branch of occult learning; and the germs of the idea which burst into full flower in the following period can be plainly traced in this.

II.

This corresponds to the Middle Ages of European history. Just as in the political events of this period the East and West were closely associated, a similar connection existed in science and literature. This, which is the period of alchemy, embraces the great names of Rhazes, Avicenna, Djabez (Geber), in the East, and the equally famous names of Albertus Magnus, Roger Bacon, Lully, and Basil Valentine in the West. It includes no fewer than seven centuries—from the eighth or ninth down to the sixteenth.

III.

At this time begins a new epoch, inaugurated by the zeal of Paracelsus—the epoch of medical chemistry. The theories of this time were of comparatively short duration. They dominated for barely two centuries, corresponding with the first two of modern history, after the Reformation. The chemists of this period were energetic and

successful, and have left their names stamped deeply on the science. Besides Paracelsus were Libarius, Glauber, van Helmont, Agricola, and many others of great ability.

IV.

This falls within the seventeenth and eighteenth centuries, and it is the first in which chemistry stands out as a definite subject, with a special field of investigation apart from applications, with a body of ascertained facts and methods, and with what may be called a general principle.

It was inaugurated by Boyle, reached its highest theoretical position in Stahl, and was concluded amidst the brilliant discoveries of Black, Cavendish, Priestley, and Scheele.

V.

A single step with Lavoisier brings us to the last period, that of modern chemistry—a science of number, weight, and measure now raised to the rank of an exact science.

Apocrypha (Wisdom of Solomon),

"For the elements were changed in themselves by a kind of harmony, like as in a psalterly notes change the name of a tune and yet are always sound; which may well be perceived by the sight of the things that have been done."—(chap. xii.).

"The fire had power in the water forgetting his own virtue: and the water forgot his own quenching nature." "On the other side the flames wasted not the flesh of the corruptible living things, though they walked therein; neither melted they the icy kind of heavenly meat, that was of nature apt to melt. For he hath given me certain knowledge of the things that are, namely, to know how the world was made and the operations of the elements."—(chap. xix.).

Ancient Egyptian Metallurgy—Rawlinson.

"Metallurgy in Egypt comprises the working in gold, in silver, and lead to a small extent, in copper, in iron, and in bronze. Tin appears to have been scarcely used except as an alloy, while zinc was wholly unknown. The Egyptians found gold in considerable quantities within the limits of their own land. The manufacture of objects out of gold was effected by goldsmiths, who after melting down an ingot or a portion of one, in a crucible, with the help of a blow-pipe, proceeded to work the material into shape with the forceps and tongs, and finally to fashion it with graving tools. Among the objects produced the commonest were solid rings of a certain size and weight, which seem to have passed current as money, vases, bowls, baskets, armlets, bracelets, necklaces, ear-rings, and other ornaments of the person, cups, goblets, rhytons, and other

* Delivered at the Royal Institution, May 19th, 1906.

drinking vessels; statuettes also were sometimes made of gold, and figures of the sacred animals were inlaid with it.

"In silver the objects produced were principally rings used for money, vases, bracelets, plates to be employed as ornaments of mummies, figures of gods and sacred animals, and finger-rings. It is worthy of observation that the silver is sometimes gilt.

"Lead objects seem scarcely to be found; and the only proof which exists of the metal being known and worked by the Egyptians is its employment as a solder in combination with tin, without which it will not serve the purpose; Egypt did not produce it, so far as appears, but it was sometimes taken as tribute from foreign nations in considerable quantities.

"It has been much questioned whether iron was employed at all by the Egyptians until the time of the Greek conquest, as but very few specimens of that metal have been found, and the date of the few iron objects discovered is very uncertain. The paucity of such instances is partially, if not wholly, accounted for by the rapid decay of iron in the nitrous earth of Egypt, or when oxidised by exposure to the air. It seems, moreover, very improbable that the Hebrews and Canaanites should for centuries have been well acquainted with the uses of iron, and their neighbours of Egypt, whose civilisation was far more advanced, have been ignorant of it.

"The manufacture of bronze was by far the most extensive branch of Egyptian metallurgy. The number of articles found of this alloy shows it must have been employed by the Egyptian metallurgists to as large an extent as all the other metals put together. The bronze was very variously composed, sometimes it contained as much as fourteen parts of tin and one of iron to eighty-five parts of copper, a very unusual proportion; more often the copper stood to the tin as eighty-five to twelve, while sometimes the proportion was as high as ninety-four to six.

"On a reference to the drawings found on the tombs in Egypt we find figures illustrating the arts of metallurgy and glass making, together with furnaces, blow-pipes, &c., but what is most interesting is that the operations were evidently conducted by weighed portions of matter, so that it is certain that the balance was employed at a very early period. We know, moreover, from Biblical history that the balance was used, for we read that 'Abraham weighed to Ephron the silver which he had named in the audience of the sons of Heth, 400 shekels of silver current with the merchant.'

*Edict of Diocletian against Alchemy, A.D. 284—306.**
(Gibbon's "Decline and Fall," Chap. xiii.)

"'He caused a diligent enquiry to be made for all the ancient books which treated of the admirable art of making gold and silver, and without pity committed them to the flames; apprehensive as we are assured, lest the opulence of the Egyptians should inspire them with confidence to rebel against the empire.' But if Diocletian had been convinced of the reality of that valuable art, far from extinguishing the memory, he would have converted the operation of it to the benefit of the public revenue. It is much more likely that his good sense discovered to him the folly of such magnificent pretensions, and that he was anxious of preserving the reasons and fortunes of his subjects from the mischievous pursuit. It may be remarked that these ancient books, so liberally ascribed to Pythagoras, Solomon, or Hermes, were the pious frauds of more recent adepts. *The Greeks were inattentive either to the use or to the abuse of chymistry.* In that immense register, where Pliny has deposited the discoveries, the arts, and the errors of mankind, there is not the least mention of the transmutation of metals, and the persecution of Diocletian is the first authentic event in the history of alchemy. The conquest of Egypt by the Arabs diffused that vain science over the Globe."

* Diocletian (Diocletianus Valerius) was elected to the purple after the assassination of Numerianus, A.D. 284; he besieged Alexandria and defeated and subdued the Egyptians.

Metals of the Ancient Greeks discovered in the Excavations at Troy, Mycenæ, &c., by Dr. Schliemann.

"Together with thousands of stone implements, I found also many of copper, and the frequently discovered moulds of mica-schist for casting copper weapons and implements, as well as the many small crucibles, and small roughly made bowls, spoons, and funnels for filling the moulds, prove that this metal was much used.

"We find copper vessels continually referred to in the Iliad, together with tripods, as prizes in the games, or as presents. But they are generally referred to in the Odyssey as basins in which the hands were washed at the sacrifice or before dinner. They were also used for the foot-bath. It deserves particular attention that three of the five copper vessels, and particularly the large can, show unequivocal marks of long use on the fire, also that there is no soldering in any one of the large copper vessels found in this or any other of the Mycenaean tombs; these large vessels consist merely of copper plates, solidly joined together with innumerable small pins. All the handles are likewise attached with broad-headed nails.

"While speaking of soldering, I may mention that Prof. Landerer informs me that the Mycenaean goldsmiths soldered gold with the help of borax (borate of soda), which is still used for the same purpose. He adds that he was lucky enough to discover this salt on the border of an ancient false medal from Ægina; that it was called in antiquity 'gold cement,' and that it was imported from Persia and India."

Pliny's View of some Marvellous Facts connected with Fire.

"Having now described all the creations of human ingenuity, reproductions, in fact, of nature by the agency of art, it cannot but recur to us with a feeling of admiration, that there is hardly any process which is not perfected through the intervention of fire. Submit to its action some sandy soil, and in one place it will yield glass, in another silver, in another minium, and in others again lead and its several varieties, pigments, and numerous medicaments. It is through the agency of fire that stones are melted into copper; by fire that iron is produced, and subdued to our purposes; by fire that gold is purified; by fire, too, that the stone is calcined which is to hold together the walls of our houses. Some materials, again, are all the better for being repeatedly submitted to the action of fire; and the same substance will yield one product at the first fusion, another at the second, and another at the third. Charcoal, when it has passed through fire and has been quenched, only begins to assume its active properties; and when it might be supposed to have been reduced to annihilation it is then that it has its greatest energies,

"An element this, of immense of boundless power, and as to which it is a matter of doubt whether it does not create even more than it destroys."

Ordeal by Fire.

One of the Pontiffs of the religion of Zoroaster, Adurbad Mabrasphand, offered to submit to the proof of fire. He proposed that they should throw over his body a quantity of molten copper at a white heat, prophesying that it should not burn him. The incredulous regarded the experiment as prodigious. It is said the trial was made with success, and that many converts were made.

Origin of Symbols of the Metals.—Beckman.

"The next question is, Why were the metals divided in the like manner among the gods, and named after them? Of all the conjectures that can be formed in answer to this question, the following appears to me the most probable.

"The number of the deified places made the number seven so sacred to the Egyptians, Persians, and other nations, that all those things which amounted to the same number, or which could be divided by it without a remainder, were supposed to have an affinity or a likeness to, and connection with each other. The seven metals, therefore, were considered as having some relationship to

the planets, and with them to the gods, and were accordingly named after them.

"To each god was assigned a metal, the origin and use of which was under his particular providence and government; and to each metal were ascribed the powers and properties of the planet and divinity of the like name: from which arose, in the course of time, many of the ridiculous conceits of the alchemists. In the character of the adepts discover gold with a silver colour.

"The mythological signification of these characters cannot be older than the Grecian mythology, but the chemical may be traced to a much earlier period."

Magic.—Ennemoser.

The term magic has come down to us from very early times, and always in close association with the priesthood. By an easy gradation we get the term magi applied to men who, while exercising the functions of the Priest, applied themselves to the acquisition of secular knowledge of all kinds.

The Magi are to be met with in the most ancient traditions of the old world. India, Persia, Chaldea, and Egypt were the cradles of the oldest magic; Zoroaster, Ostanes, the Brahmins, the Chaldean sages, and the Egyptian priests were the primitive possessors of its secrets. It must be admitted their knowledge was used to the furtherance of human happiness; justice, truth, and the power of self-sacrifice being the qualities with which they are endowed; the neglect of any one of these virtues was punished in the most cruel manner. From Pliny we learn that magic was early associated with medicine, though the common belief was that it included all occult science; later under this title was understood enchantment and any extraordinary operations, such as making gold, exorcising spirits, &c.

Among the supernatural powers was reckoned that of predicting the future, and that of acting directly upon others even at a distance; and on this account magic may be separated into seeing and acting. The original description was, in fact, grounded on this aphorism: "Man may become, by this assistance and co-operation of spiritual powers, and the capacities of his higher divine origin, capable of a higher sphere of activity as well without as within himself, which gives him dominion over his own, and over surrounding nations."

We have no immediate and authentic source to which we may refer for the myths and mysteries of the ancient nations. Among the Egyptians and Orientals, we find but fragments, though in such numbers that we are able to decide that it is among the nations of the East that we must search for earlier traces, and even for their origin. According to the latest investigations, the very earliest records are to be met with in the Zendavesta, the Laws of Manu, and the Jewish Traditions of the Cabbala. Of the latter it is interesting to take a nearer view, and examine some of its principal teachings which are not alone of importance to theology, but to philosophy in general, and magic in particular. Inquiries instituted in our own time have shown, at all events, that the traditions of Judaism belong to the earliest sources of the mysteries. Schelling suggests that in the Grecian mythology the ruins of a superior intelligence and even a perfect system are to be found, and further, that possibly some portions of the system might be discovered in the Jewish philosophy, or the so-called Cabbala. Many references to this Hebrew source may be traced in early writers; indeed, the greater part of the writings of the Middle Ages were probably but continuations of that which had already been borrowed from the Cabbala, although Johannes Scotus Erigena, Albertus Magnus, Raymond Lully, and others appear to have prosecuted individual inquiries. Later we find many inquirers in this fruitful field of research. The philosophies of Agrippa, of Paracelsus, of Van Helmont, and Jacob Böhmen, all bear striking resemblance to the Jewish teachings. Of this latter, a recent writer made this startling assertion, that "in Böhmen's writings is to be

found the true and clear demonstration of every physical fact that has been discovered since his day."

According to the Cabbala, there exists, besides angels, intermediate spirits—the spirits of the elements—the *Schedim* of the Jews, and divided into four classes, the chief of whom is Asmodi. The first class contains the spirits of the fire; the second of fire and water; the third of fire, air, and water; the fourth have a mineral ingredient. This is completely the doctrine of Paracelsus. The spirits of the two last classes are possessed mostly of evil natures, and are fond of causing injury to man. The other two are possessed of greater wisdom, and knowing many of the secrets of nature, willingly disclose them to man. According to the Cabbala, everything that exists, whether great or small, stands in a magical union with the rest of nature. Everywhere is the external the operation of the internal, and the external reacts upon the internal; thus the stars have as great an influence upon man as upon the whole of nature; for the constellations presiding at the birth of a child determine its physical and mental qualities. These extracts are sufficient to give an idea of the contents of the Cabbala with regard to magic, which it treats of in all its ramifications, containing that which became Christian mysticism, and the magic of the Middle Ages.

Transmutation of Metals and Astrology.—Godwin.

"In proportion as the pursuit of transmutation and the search after the elixir of immortality grew into vogue, the adepts became desirous of investing them with the venerable garb of antiquity. They endeavoured to carry up the study to the time of Solomon; and there were not wanting some who imputed it to the first father of mankind. They were desirous to track its footsteps in ancient Egypt, and they found a mythological representation of it in the expedition of Jason after the Golden Fleece, and in the caldron by which Medea restored the father of Jason to his original youth. But, as has already been said, the first unquestionable mention of the subject is to be referred to the time of Diocletian.

"The art, as we have said, is in its own nature sufficiently mystical, depending on nice combinations and proportions of ingredients, and upon the addition of each ingredient being made exactly in the critical moment, and in the precise degree of heat, indicated by the colour of the vapour arising from the crucible or retort. This was watched by the operator with inexhaustible patience; and it was often found or supposed that the minutest error in this respect caused the most promising appearances to fail of the expected success. This circumstance, no doubt, occasionally gave an opportunity to an artful impostor to account for his own miscarriage and thus to prevail upon his credulous dupe to enable him to begin his tedious experiment again.

"But besides this, it appears that those whose object was the transmutation of metals very frequently joined in this pursuit the study of astrology, and even the practice of sorcery. So much delicacy and nicety were supposed to be required in the process for the transmutation of metals, that it could not hope to succeed but under a favourable conjunction of the planets; and the most flourishing pretenders to the art boasted that they had also a familiar intercourse with certain spirits of supernatural power, which assisted them in their undertakings, and enabled them to penetrate into things undiscoverable to mere human sagacity and to predict future events."

"The supposed science of astrology is well worthy of attention, if for no other reason, because it has prevailed in almost all nations and ages of the world, and has been assiduously cultivated by men frequently of great talent, and who were otherwise distinguished for the soundness of their reasoning powers, and for the steadiness and perseverance of their application to the pursuits in which they engaged. The whole of the question was built upon the supposed necessary connection of certain aspects and conjunctions or oppositions of the stars and heavenly bodies,

with the events of the world and the characters and actions of men. The human mind has ever confessed an anxiety to pry into the future, and to deal in omens and prophetic suggestions, and, certain coincidences having occurred, however fortuitously, to deduce from them rules and maxims upon which to build an anticipation of things to come. The general belief in astrology had a memorable effect on the history of the human mind. Men, so far as they are believers in astrology, look to the stars, and not to themselves, for an account of what they shall do, and resign themselves to the omnipotence of a fate which they feel it in vain to resist. Of consequence a belief in astrology has the most unfavourable tendency as to the morality of man; and, were it not that the sense of the liberty of our actions is so strong that all the reasonings in the world cannot subvert it, there would be a fatal close to all human dignity and all human virtue."

The Elements of the Alchemists and Alchemy.—Liebig.

"In the spirit of the earlier philosophy which ascribed all causes of action not perceptible by the senses to invisible spirits, and all sensible properties to tangible and material causes, common sulphur and quicksilver were regarded at first as actual constituents of the metals; certain properties were believed to be dependent on their presence, exactly as, at a more recent period, the causticity of lime and the alkalies was ascribed to the caustic or caustic principle, the peculiar smell of certain bodies to the spiritus rector, and the acidity of the acids to a primitive or original acid."

"In the ideas of the alchemists, actual sulphur and mercury were gradually supplanted by an ideal sulphur and an ideal mercury; things which combined in themselves a certain number of properties. These ideal bodies, at a later period, took the form of elementary qualities. Many bodies possessed the property of being volatile, without alteration in their other properties, when exposed to fire.

"They were sublimable, like arsenic, or capable of being distilled, like mercury. Another class of bodies was also volatile, but underwent a change in the fire, such as sulphur. A third class, although changed in the fire, was not volatile, but fixed, like the salts found in ashes. Sulphur, mercury (arsenic), and salt became at last, as has been stated, abstract conceptions, simple elements, in the sense of the four elements of Aristotle.

"As we speak of the form and shape of a thought, without understanding by these figurative terms a bodily shape, so did men in those days express abstract notions by terms indicating bodily or material things, without understanding thereby anything more than properties."

"The chemical elements of the early philosophers could not, it is obvious, be obtained in a separate form, because they were merely terms, denoting qualities alone. No one thought of obtaining them: they were regarded as constituents of all bodies."

"In order to attain that knowledge of chemistry which we now possess, it was necessary that thousands of men, armed with all the science of their respective periods, and inspired with an unconquerable ardour, with a passion for knowledge, which in its violence bordered on madness, should devote life, fortune, and their whole faculties, to the task of exploring the earth in all directions.

"It was necessary that, with indefatigable perseverance and constancy, these men should bring into contact all known substances, organic and inorganic; it was necessary that these labours should be continued for fifteen centuries. There was, finally, a mighty, an irresistible charm which urged men to devote themselves with an amount of patience and perseverance altogether unexampled in history to labours which did not tend to supply any want peculiar to the time in which they lived. This mighty impulse was nothing else than the desire for earthly happiness. By a wonderful and wise dispensation there was implanted in the minds of the wisest and most experienced men the idea of the existence of a thing, hid in the bowels of the earth, by the discovery of which man might become possessed of

those things which imply the gratification of the utmost desires of a refined sensuality—namely, gold, health, and long life, 'Gold gives power; without health there is no enjoyment, and longevity here takes the place of immortality.'—*Goethe*.

"It is the prevailing ignorance of chemistry, and especially of its history, which is the source of the very ludicrous and excessive estimation of ourselves, with which many look back on the age of alchemy; as if it were possible, or even conceivable, that for more than a thousand years the most learned and acute men, such as Francis Bacon, Spinoza, and Leibnitz, could have regarded as true and well founded an opinion void of all foundation. On the contrary, must we not suppose, as a matter beyond a doubt, that the idea of the transmutability of metals stood in a most perfect harmony with all the observations, and all the knowledge of that age, and in contradiction to none of these?

"In the first stage of the development of science, the alchemists could not possibly have any other notions of the nature of metals than those which they actually held. No others were admissible or even possible; and their views were consequently, by natural law, inevitable. Without these ideas chemistry could not now stand in its present perfection; and in order to call that science into existence, and in the course of 1500 or 2000 years to bring it to the point which it has now reached, it would have been necessary to create the science anew.

"We hear it said that the idea of the philosopher's stone was an error; but all our views have been developed from errors, and that which to-day we regard as truth in chemistry may, perhaps, before to-morrow, be regarded as a fallacy. Every theory which urges men to labour and research, which excites acuteness and sustains perseverance, is a gain to science; for it is labour and research which lead to discoveries.

"Alchemy was never at any time anything different from chemistry.

"It is utterly unjust to confound it, as is generally done, with the gold-making of the sixteenth and seventeenth centuries. Among the alchemists there was always to be found a nucleus of genuine philosophers who often deceived themselves in their theoretical views; whereas the gold-makers properly so called knowingly deceived both themselves and others.

"Alchemy was the pure science, gold-making included all those processes in which chemistry was technically applied. The achievements of such alchemists as Glauber, Böttger, and Kunkel, in this direction, may be boldly compared to the greatest discoveries of our century.

"But to return to alchemy. In judging of it we are but too apt to forget that a science represents a spiritual organism, in which, as in man, self-consciousness first appears at a certain stage of its development. We now perceive that all the special objects pursued by the alchemists have contributed to the attainment of a higher end than that of which they were conscious. The path which has led to this result was obviously the best.

"To build a palace, we require many stones, which must be quarried, and many trees which must be felled and hewed; but the plan comes from above, and is known to the architect alone.

"The philosopher's stone, for which the ancients sought with a dim and ill-defined impulse, was in its perfection nothing else than science of chemistry.

"Is that not the philosopher's stone which promises to increase the fertility of our fields and to insure the prosperity of additional millions of mankind? Does not chemistry promise that, instead of seven grains, we shall be enabled to raise eight or more on the same soil?

"Is that science not the philosopher's stone which changes the ingredients of the crust of the earth into useful products, to be further transformed by commerce into gold?

"Is that knowledge not the philosopher's stone which promises to disclose to us the laws of life, and which must

finally yield to us the means of curing diseases and of prolonging life?

"Every new discovery opens up wider and richer fields to our researches; and in the laws of nature we are still ever seeking the 'virgin earth' of the alchemists, a search which can never have an end."

(To be continued).

ON THE OSMOTIC PRESSURES OF SOME CONCENTRATED AQUEOUS SOLUTIONS.*

By the Earl of BERKELEY and E. G. J. HARTLEY.

THIS communication gives an account of measurements of osmotic pressures of aqueous solutions of cane-sugar, dextrose, galactose, and mannite. The method adopted is that briefly outlined by us in *Proc. Roy. Soc.*, vol. lxxiii. A gradually increasing pressure is placed upon the solution (which is separated from the solvent by a semi-permeable membrane) until the solvent, which at first flows into the solution, reverses its direction, and is squeezed out. The pressure, when there is no movement of the solvent, is considered to be the osmotic pressure. Owing to the difficulty of determining the exact point at which no movement takes place and for other reasons, the experiments are carried out so as to enable an observation to be made of the rate of movement of the solvent, both when the pressure on the solution is just below and when just above the turning point pressure. The osmotic pressure is deduced from these rates.

The range of pressures covered by the experiments is from 12 to 135 atmospheres.

A description is also given of the methods adopted for making the copper ferrocyanide membranes, and it is pointed out that with the best membranes, in most cases, a small quantity of solution comes through during the experiment. It is shown that even a small leak causes a considerable lowering of the observed pressure; hence the final results accepted are those where the leak was least.

Attention is drawn to the fact that the osmotic pressures of cane-sugar solutions when measured directly and when calculated from their vapour pressures agree to within 3 per cent.

ELECTRO-CHEMICAL CALCULATIONS.†.

By JOSEPH W. RICHARDS.

ELECTRO-CHEMICAL processes produce chemical changes through the agency of the electric current, and the current is used primarily either for its electrolytic effect or for its thermal effect. The first thing needful, in order to make any calculations connecting electric energy with thermal or chemical effect, is to set forth the values of electric energy as expressed in thermal or mechanical units, in order to get a common energy basis on which to make comparisons, and to postulate the facts concerning the electrolytic effect of the electric current.

ENERGETICS OF THE ELECTRIC CURRENT.

One watt-second of electric energy may be postulated as equivalent to one joule of mechanical work, or 0.2385 grm.-calories. This is the energy basis on which electric and chemical phenomena meet on common ground, for the only energy measure of chemical reaction which has as yet been quantitatively investigated is the thermal one. We therefore express the energy of a chemical reaction in the terms in which that energy has been measured, and then have the theoretical bases for calculating the amount of electrical current which can theoretically furnish that amount of thermal energy.

PRINCIPLES OF THERMO-CHEMISTRY.

The measuring of the amount of heat liberated or absorbed in chemical combination or decomposition or reaction is the province of thermo-chemistry. Many enthusiastic scientists have accumulated large numbers of these experimental data, from which, however, very few generalisations have been, up to the present, deduced. There are critical discussions of thermo-chemical data for inorganic compounds in Ostwald's "Allgemeine Chemie"; one can find the most complete collection of thermo-chemical figures yet published, both for inorganic and organic compounds, in Berthelot's "Thermochemie"; in English, Muir's "Elements of Thermal Chemistry" is the only collection of tables on this subject which aims at completeness, and the work is at present nearly two decades old. More or less incomplete or fragmentary tables can be found in works on chemistry or treatises on heat. In giving the data, chemists always give the heat change for molecular weights of the substances concerned; for instance, $(\text{H}_2, \text{O}) = 69,000$ calories means that when two parts of hydrogen unite with sixteen parts of oxygen to form eighteen parts of water, 69,000 heat units are evolved. If the weights of the substances be called kilograms., the heat units are kilogram.-calories; if called grms. they are grm.-calories; if called ounces or pounds, they are ounce- or pound-calories (1°C.). The Germans write the above $(\text{H}_2, \text{O}) = 690 \text{ K}$, in which K stands for 100 ordinary heat units, while the French write it $(\text{H}_2, \text{O}) = 69.0 \text{ cal.}$, in which the weights of the substances are supposed to be taken in grms., and the heat evolved expressed in kilogram.-calories. In our opinion, the English style first given is logically and practically superior to the other two, and is the best to follow.

It must be borne in mind that, almost without exception, the thermo-chemical data given in the tables are those which have been determined starting with the constituents at laboratory temperature and ending with the products at the same, or very nearly the same, temperature. The heat quantities therefore apply strictly only to electro-chemical processes taking place at ordinary temperature, or very near thereto, and with the constituents or products in the same physical state as was used in the calorimetric determination. If the electro-chemical process is taking place at any different temperature, let us call it $t^\circ \text{C.}$, and the ordinary temperature 15°C. , the heat of the chemical change at t° , from constituents at t° to products at t° , or *vice versa*, can be calculated from the rather simple rule, that:—

The heat of combination at t° equals the heat of combination at 15° (tabulated heat), plus the heat necessary to raise the constituents from their ordinary state at 15° to their ordinary state at t° , and minus the heat which would be necessary to raise the products from their ordinary state at 15° to their ordinary state at t° .

The above calculation requires a knowledge of the specific heats and latent heats of change of state of the constituents and of the products of the reaction, between 15° and t° , but when these are known, the heat of the reaction at t° , the quantities very often needed in electro-chemical calculations, can be evaluated. These specific heats and latent heats are best obtained from such standard works as Landolt and Bornstein's "Physikalisch-chemische Tabellen," or works of similar scope in English.

FARADAY'S LAWS.

There is another and an entirely different quantitative relation between the amount of electric current used and the quantity of electro-chemical action produced, which applies to direct current producing electrolysis. In this case, while the energy relations hold, yet they are conditioned by the fact that every coulomb of electricity passing produces a definite amount of chemical change, equivalent to the setting free of a certain weight of hydrogen, for instance, and the energy required must adjust itself to the bringing about of this amount of chemical change. I am referring, of course, to Faraday's

* Abstract of a Paper read before the Royal Society, June 7, 1906.

† From the *Journal Franklin Institute*, February and March, 1906.

discoveries, which may be briefly summed up in the two statements that:—

1. The amount of chemical change produced electrolytically by the current is proportional only to the amount of electricity passing, as measured in coulombs, and is independent of the strength or temperature of the electrolyte, or the size or distance apart of the electrodes.

2. The amount of different elements dissolved or set free by the passage of a given amount of electricity proportional to their chemical equivalents.

When it was determined experimentally that 0.0001035 gm. of hydrogen is set free by one coulomb, or that 96,540 coulombs set free one chemical equivalent, 1 gm., of hydrogen, the whole scale of relations for all elements whose chemical equivalents were known, became known. The "Faraday," 96,540 coulombs, sets free, or tends to set free, in passing from an anode to a cathode, a chemical equivalent weight in grms. of any element. No law of nature has been subjected to more rigorous tests than this law of Faraday, and it appears so far as a law without an exception.

EVOLUTION OF GAS ELECTROLYTICALLY.

A Faraday of current 96,540 coulombs (representing 26.82 ampère hours) sets free 1 gm. equivalent of metal or acid element or radical. If the element or acid radical is gaseous, there is a simple relation between the current flow and the volume of gas evolved, based on the observation that a gm. equivalent of a monatomic gaseous element has a volume under standard conditions of temperature and pressure of 22.22 litres, of a diatomic gaseous element, of 11.11 litres, &c. Thus, 96,540 coulombs set free a gm. equivalent weight of hydrogen, chlorine, sodium, zinc, &c. The formulæ for these in the gaseous state are Na, Zn, H₂, Cl₂; the molecules of these gases, representing 22.22 litres, contains therefore:—

Na molecule—1 gm.-equivalents	
Zn " —2 " "	"
H ₂ " —2 " "	"
Cl ₂ " —2 " "	"
O ₂ " —4 " "	"

Therefore, 1 Faraday (26.82 ampère hours) sets free 1 gm. molecule of sodium vapour (22.22 litres), and $\frac{1}{2}$ a gm. molecule (11.11 litres) of vapour of zinc, hydrogen gas or chlorine gas, assumed at normal temperature and pressure. For any other temperature, t , or pressure, p , in m.m. of mercury, the volume would be:—

$$\text{Standard volume} \times \frac{273 + t}{273} \times \frac{760}{p}$$

Example.—How much oxygen and hydrogen should be produced per day by 300 ampères passing through 20 cells in series?

Solution.—The ampère hours performing electrolysis are—

$$300 \times 20 \times 24 = 144,000.$$

The Faradays' passing are—

$$144,000 \div 26.82 = 5370.$$

The volumes of gas produced will therefore be—

$$5370 \times 11.11 = 59,670 \text{ litres of hydrogen.}$$

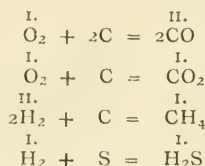
$$5370 \times 5.55 = 29,835 \text{ litres of oxygen.}$$

If the gas evolved is a compound gas or acid radical, which is formed at the electrodes, the valence of the acid of basic constituent in a molecule of the gas is the basis of calculation. For instance, CO, CO₂, CH₄, H₂S all represent molecules of the said gases, of a volume of 22.22 litres, and contain respectively:—

CO contains 2 gm.-equivalents of oxygen	
CO ₂ " 4 " " " "	"
CH ₄ " 4 " " " "	"
H ₂ S " 2 " " " "	"

One Faraday (26.82 ampère hours) which would produce 1 gm.-equivalent of oxygen or hydrogen, would therefore produce half a molecule (11.11 litres) of CO or H₂S, or quarter of a molecule of CO₂ or CH₄ (5.55 litres).

Another means of calculating the volume of these gases is to note that CO₂ and H₂S are equal in volume to the oxygen or hydrogen contained in them, CO is double the volume of the oxygen contained in it, and CH₄ is double the volume of the hydrogen going into its composition; so that the volumes of the compound gases can be calculated from the volumes of the simple gases going into their formation. The relations alluded to are shown by the Roman numerals indicating molecules or volumes in the following equations:



OHM'S LAWS.

The resistance which the electric current encounters to its flow through the body of a substance is determined by the specific resistivity of the body per unit cube of substance, multiplied by its length and divided by its cross-sectional area. The specific resistivity is given in tables per centimetre cubed, in ohms, and the simple arithmetic described gives us the resistance of any bar or wire of said material. The resistance of the body being known, Ohm's laws furnish us with the relation between the applied voltage and current flow through the body as follows:—

$$\text{Current} = \frac{\text{potential drop}}{\text{resistance}},$$

or—

$$\text{Ampères} = \frac{\text{volts drop}}{\text{ohms resistance}}.$$

These relations apply to the current in the body of an electrolyte just as strictly as to a metallic wire (and tables of specific resistivity of electrolytes are given in almost all books on electro-chemistry), but they do not apply at all to the resistance or drop of potential at the surface of an electrode; that is, at the contact surface where current enters or leaves an electrolyte. (Kohlrausch and Holborn's "Leitungsfähigkeit der Elektrolyte" is the most complete collection of such data). That latter potential drop is due to chemical work being performed, and has no connection whatever with ordinary ohmic resistance and Ohm's laws.

RESISTANCE CAPACITY OF VESSELS.

In making electro-chemical experiments, as in tubes or in vessels between fixed electrodes, it is often convenient to calculate, as a constant of the apparatus, the "resistance capacity" of the vessel. This is simply its ohmic resistance, between the two fixed electrodes, supposing it to be filled with a liquid whose specific resistance is unity. If the cross section is uniform, and the electrodes of similar area, this resistance capacity would be in ohms, supposing the measurements made in centimetres:—

$$\text{Resistance capacity} = \frac{\text{length between electrodes}}{\text{cross sectional area of electrolyte}}.$$

Thenceforth, if said vessel is filled between the electrodes with a liquid whose specific resistance is known, the ohmic resistance of the electrolyte will be simply the product of the resistance capacity by the specific resistance of the given liquid used; that is, ohmic resistance of electrolyte = resistance capacity of the vessel $\times$ specific resistance of electrolyte.

DETERMINATION OF OHMIC RESISTANCE.

If the conductor is not electrolysed by the current, its resistance is measured by sending a known current through it and measuring the drop of potential at its terminals.

$$\text{Resistance (in ohms)} = \frac{\text{potential drop (in volts)}}{\text{current flowing (in ampères)}}$$

The current used may be either direct or alternating, the former is preferable because of the more accurate measurements possible. Another method, not so often used, but applicable under many circumstances, is to put a delicate thermometer or thermo-couple in contact with the conductor and measure the rate at which its temperature begins to rise. Knowing its specific gravity (weight of 1 c.c. in grms.) and its specific heat (per unit of weight), the heat generated per second in 1 c.c. is known:—

$$\text{Heat generated (grm. calories)} = \text{specific gravity} \times \text{specific heat} \times \text{rise of temperature per second.}$$

But this quantity is also equal to the heat value of the current used, which is 0.2385 times the watts used, or 0.2385 times the square of the current used into the resistance. We therefore have:—

$$\text{Resistance (in ohms)} = \frac{\text{heat found calorimetrically}}{0.2385 \times (\text{current used})^2}$$

The above method is particularly applicable to electrolytes of any kind if they are placed in a long tube of low heat-conducting material, and the rise of temperature thus measured at a point remote from the electrodes. Then, whatever action, chemical or thermal, occur at the electrodes, and whatever potential drop may occur, it is only necessary that the amount of current passing be accurately measured, the specific heat and specific gravity of the electrolyte be known, and the rate of rise of temperature be measured at the first few seconds after turning on the current, to be able to calculate the specific resistance.

The use of alternating current for measurements of ohmic resistance using Kohlrausch's method of Wheatstone bridge and a telephone is applicable with accuracy to non-electrolytic conductors, and has generally been assumed to be applicable quite as accurately to electrolytes. Recent work on the possibility of electrolysis occurring when alternating current is passed through an electrolyte has rather cast doubts upon the accuracy of these tests. It is possible that most determinations thus made have been free from error, but we can understand now that tests so made might be erroneous in many instances, if made with certain electrodes and with certain frequency of alternation of the measuring current.

For many practical purposes, the ohmic resistance of an electrolytic cell can be determined by the following simple device and calculation:—Use electrodes equal to the cross section of the electrolyte, and put in series with a relatively high resistance, so as to keep the strength of current as nearly constant as possible. Measure ampères and voltage drop with the plates as wide apart as possible; draw together till they are exactly half the distance apart, and measure again. If the outside resistance is high enough, the ampères will be constant within the ability of the ammeter to record, while the voltage will decrease. Double the decrease in voltage will be the total voltage drop in overcoming the ohmic resistance of the whole cell. Designating this as the voltage drop due to electrical conductivity of the electrolyte, V_c , we have:—

$$\text{Resistance of cell (in ohms)} = \frac{V_c}{\text{ampères passing}}$$

(To be continued).

Rapidity of Absorption of Odours by Milk.—F. Bordas and M. Toutplain.—The authors perform a series of experiments on the rapidity of absorption of formic aldehyde vapours by milk.—*Comptes Rendus*, cxlii., No. 22.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 21st, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

PROF. T. E. THORPE, F.R.S., delivered the Cleve Memorial Lecture. A vote of thanks to the lecturer was proposed by Sir HENRY E. ROSCOE, seconded by Prof. TILDEN, and carried by acclamation.

The PRESIDENT announced that the Council had awarded the Longstaff medal to Prof. W. N. Hartley, F.R.S., in recognition of his spectrochemical investigations; the presentation will be made at the first meeting of the new session, Thursday, October 18th, at 8.30 p.m.

Messrs. H. G. F. Micklewright and J. S. Hills were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Samuel Field, 53, Whitburn Road, Lewisham, S.E.; Frederick James Harris, 1, Alexandra Terrace, Bath Road, Exeter; Archibald McArthur Johnston, Box 108, Germiston, Transvaal, South Africa; Emmanuel Isaac Thorne, 13, Cantwell Road, Plumstead, S.E.; Frederick William Watson, B.Sc., P.O. Box 108, Germiston, Transvaal, South Africa.

A certificate has been authorised by the Council for presentation for ballot under By-law I. (3) in favour of Dr. Charles H. Hertz, Chapel Hill, North Carolina, U.S.A.

Of the following papers, those marked * were read:—

*124. "*The Constituents of the Essential Oil from the Fruit of Pittosporum undulatum.*" By FREDERICK BELDING POWELL and FRANK TUTIN.

The oil employed in this investigation was freshly distilled for the purpose in Australia. From 220 kilogrms. of the nearly ripe fruit, gathered during December and January, 960 grms. of oil were obtained, corresponding to a yield of 0.44 per cent. The essential oil is pale yellow, and has a pleasant odour resembling that of orange oil. Its constants were as follows:— $d_{15}^{15} = 0.8615$; $n_D^{20} + 74.4'$ in a 1-dcm. tube. It was insoluble in ten times its volume of 70 per cent alcohol.

The results of the investigation have shown that Pittosporum oil contains the following substances:—*d*-Pinene (nitrosochloride, nitrobenzylamine, m. p. 123°), about 4 per cent; *d*-limonene (tetrabromide, m. p. 104°), about 75 per cent; esters of valeric, formic, and other acids, a small amount; an optically inactive sesquiterpene (b. p. 263–264°, corr.; $d_{15}^{15} = 0.9100$; $n_D^{20} = 1.5030$; molecular refraction, 66.22), about 15 per cent; palmitic acid and an undetermined phenol in very small amount, and apparently a trace of salicylic acid.

The sesquiterpene contained in this oil is a slightly viscous liquid, having a pale straw colour and a delicate rose-like fragrance. Although it was not possible to obtain from it any solid derivative, such as the hydrochloride, nitrosochloride, nitrosite, or nitrosate, and thereby definitely characterise it, it is evidently not identical with either of the previously known optically inactive sesquiterpenes, humulene and limene (*Trans.*, 1895, lxvii., 60, 780; and 1904, lxxxv., 416), and may therefore be regarded as a compound which has not hitherto been described. Its molecular refraction indicates that it belongs to the group of dicyclic sesquiterpenes with two ethylenic linkings.

*125. "*Mobility of Substituents in Derivatives of β -Naphthol.*" By JOHN THEODORE HEWITT and HERBERT VICTOR MITCHELL.

The authors found that when *p*-nitrobenzenediazonium chloride was added to an alkaline solution of 1-bromo-2-naphthol, coupling immediately occurred. The resulting substance when purified was free from halogen, and on analysis proved to be identical with *p*-nitrobenzenazo- β -naphthol; the bromine atom had consequently been dis-

placed by the benzene group. The generality of the reaction was shown by examining the behaviour of the corresponding chloro- and iodo- β -naphthols, whilst alkaline bromonaphthol was also treated with diazotised solutions of the following amino-compounds:—*o*-, *m*-, and *p*-Toluidines, *o*- and *m*-nitroanilines, 2:4-dinitroaniline, *p*-phenetidine, *o*- and *p*-aminobenzoic acids, β -naphthylamine, and the 6- and 8-monosulphonic derivatives of the latter base.

Incidentally, the acetyl-derivative of 1-bromo- β -naphthol was prepared; this proved to be a well-crystallising solid, m. p. 56° , and not an oil, as described by Canzoneri (*Gazzetta*, 1882, xii., 431).

The nitroso-group in nitroso- β -naphthol is also mobile, treatment with nitric acid furnishing 1:6-dinitro-2-naphthol.

DISCUSSION.

Mr. W. A. DAVIS referred to his results, summarised in the Reports for 1900 to 1903 of the Committee of the British Association on Isomeric Naphthalene Derivatives, showing the mobility of a halogen atom in position 1 in β -naphthol under the influence of hydriodic acid or nitric acid. Halogen atoms in other positions in the nucleus were not affected, and the same was true of an α -halogen in a non-hydroxylated naphthalene nucleus. The sensitiveness of the α -halogen atom in the naphthol was to be attributed to the formation of an additive compound at the $\alpha\beta$ -ethenoid linking, as was well illustrated in the case of nitric acid by the production of the nitro-bromo-keto-compounds.

Dr. HEWITT, in replying to the President, remarked that he had not encountered any statement concerning the displacement of halogen atoms by azo-groups. The product of the action of diazotised aniline on an alkaline solution of bromo- β -naphthol, though very tarry, evidently contained some benzeneazo- β -naphthol, since if nitrated in concentrated sulphuric acid solution a certain amount of *p*-nitrobenzeneazo- β -naphthol could be isolated.

Mr. DAVIS's experiments on the action of hydriodic acid on α -halogen-substituted β -naphthols seemed to be of a different nature, in that the compounds were reduced; it was not the direct replacement of negative atoms by other complex groups.

*126. "The Decomposition of Nitrocellulose." By OSWALD SILBERRAD and ROBERT CROSBIE FARMER.

Great uncertainty has hitherto prevailed as to the products which result from the gradual deterioration of nitrocellulose. An exhaustive examination of the decomposition products obtained on storage of 100 kilograms of gelatinised nitrocellulose for twenty-three weeks at 54 – 55° in a damp atmosphere led to the identification of the following products:—Ethyl nitrate, ethyl nitrite, ethyl alcohol, nitric and nitrous acids, ammonia, formic, acetic, butyric, dihydroxybutyric, oxalic, tartaric, isosaccharinic, and hydroxypyruvic acids. Carbohydrates were also present.

*127. "Note on Gunpowder and Bullets, made about 1641, Recently Discovered in Durham Castle." By OSWALD SILBERRAD and WILLIAM SLESSOR SIMPSON.

For the materials for this investigation we are indebted to the Secretaries of this Society for putting us into communication with J. T. Johnson, Esq., of Durham School, who kindly forwarded samples of the bullets and gunpowder in question. The ammunition was found in a bucket which had been walled up in the roof of Durham Castle, probably having been placed there about 1641, when the Castle was armed against a Scottish raid.

The bullets consisted of roughly moulded spheres of lead of two different sizes, some being 1.5 c.m. and others 1.8 c.m. in diameter. On analysis they were found to consist of 99.17 per cent of lead, and to contain a small quantity of iron and silver together with traces of bismuth, arsenic, and antimony.

The gunpowder, on analysis, was found to approximate closely in composition to the black powder now used in this country. In appearance, however, it differed widely from powder manufactured at the present day, the in-

gredients having been merely ground and mixed together, no attempt at granulation having been made.

	Analysis of powder from Durham Castle.		Proportions used at present time in this country.
	On sample.	On dry material.	
Potassium nitrate	73.99	74.81	75
Carbon . . .	14.71	14.87	15
Sulphur . . .	9.98	10.09	10
Moisture . . .	1.10		
	99.78		

These results are somewhat surprising, since the compositions used in this country during the seventeenth century all contained a much higher percentage of sulphur. It seems indeed probable that this powder was of Prussian origin, Prussian musket powder being the only explosive of this composition in use at that date.

The calorimetric value was determined by firing a charge at a density of loading 0.48 in a closed vessel suspended in a calorimeter.

The pressure recorded was 9.7 tons per sq. in., or 1478 atmospheres. The calorimetric value = 694 calories per gram.

This is in close agreement with the figure given by ordinary black powder.

The critical time of burning was determined at a density of loading of 0.230. The apparatus used was similar to that described by Sir Andrew Noble (*Phil. Trans.*, 1905, ccv., 201). The pressure was, however, taken on a crusher copper, and the time measured by means of a calibrated tuning-fork, which was simultaneously made to plot a record on a revolving drum.

The pressure recorded at this density was 4.51 tons per sq. inch, 687 atmospheres; ordinary black powder fired at this density gives a pressure of 686 atmospheres (Sir Andrew Noble, *Phil. Trans.*, 1905, ccv., 15). The critical time of burning observed was 0.0030 second. This is more rapid than that of the granulated powders now in use.

Unfortunately, we were debarred from carrying out further experiments at higher densities owing to the small amount of material at our disposal.

128. "The Constitution of Acetone." By MILLICENT TAYLOR.

The action of sodium and of magnesium methyl iodide on acetone has been studied. So-called "sodium acetone," the product of the action of sodium on highly dilute acetone, is shown to consist of a mixture of caustic soda with a small proportion of sodium isopropoxide; this is deduced from the percentage of sodium in the substance, and also from its behaviour with acid chlorides.

The only esters obtained by the action of chloroformic ester and *p*-nitrobenzoyl chloride on "sodium acetone" are ethyl isopropyl carbonate and isopropyl-*p*-nitrobenzoate respectively.

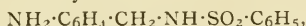
In no case was any indication of the formation of isopropenyl esters obtained. Moreover, in one case in which the yield of each product was determined, it was found that the total acid chloride employed was converted into acid anhydride, acid (or sodium salt), and isopropyl ester, leaving no possibility of the formation of other esters.

By the action of acetone on magnesium methyl iodide at the ordinary temperature and up to 140° no methane was liberated.

These results prove that acetone does not behave, either towards sodium or Grignard's reagent, as isopropenyl alcohol, $\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}_2$, and also that it does not contain any hydrogen directly replaceable by sodium under the conditions investigated.

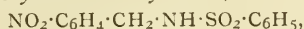
129. "Diazo-derivatives of the Mixed Aliphatic Aromatic ω -Benzenesulphonylamino benzylamines." By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

A study of the action of nitrous acid on the benzenesulphonylaminobenzylamines,—

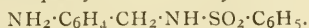


showed that diazoimides could be obtained from the ortho- and meta-compounds, but not from the para-isomeride.

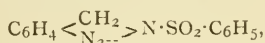
o-Nitrobenzylamine was converted successively into benzenesulphonyl-*o*-nitrobenzylamine,—



and *ω*-benzenesulphonyl-*o*-aminobenzylamine,—



This acylated diamine, when diazotised in strong hydrochloric acid, yielded a soluble diazonium salt; this substance, on treatment with aqueous sodium acetate, furnished a colourless mixed *diazoimide*,—



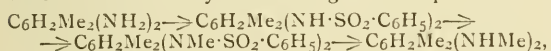
which, like the yellow aromatic para-diazoimides, is reconverted into the diazonium salt by the action of cold concentrated hydrochloric acid.

ω-Benzenesulphonyl-*m*-aminobenzylamine also gave rise to a soluble diazonium salt which, although not affected by aqueous sodium acetate, underwent condensation in the presence of excess of potassium bicarbonate, and furnished a pale yellow *diazoimide* isomeric with the preceding compound.

These diazoimides owe their formation to the presence of hydrogen in the acylamino-group, $\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$, for when this atom is replaced by methyl, condensation does not occur. The three benzenesulphonylaminobenzylamines and the methyl derivatives of the ortho- and meta-bases all yielded azo-*β*-naphthol derivatives.

130. "Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds. Part V. *s*-Dimethyl-4 : 6-diamino-*m*-xylene." By GILBERT THOMAS MORGAN and ARTHUR CLAYTON.

s-Dimethyl-4 : 6-diamino-*m*-xylene (m. p. 100–101°), which was obtained by the following series of operations:—



yielded a colourless *dinitrosoamine*, $\text{C}_6\text{H}_2\text{Me}_2(\text{NMe}\cdot\text{NO})_2$, and on treatment with *p*-nitrobenzenediazonium chloride gave rise to a small amount of the *aminoazo*-compound, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{HMe}_2(\text{NHMe})_2$, which separated from benzene either in brownish grey crusts or in dark red prisms or diamond-shaped plates melting at 218°. This result shows that the symmetrical dimethylation of 4 : 6-diamino-*m*-xylene does not inhibit the production of an orthoazo-derivative.

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.

(LONDON SECTION).

Ordinary Meeting, June 11th, 1906.

Mr. A. G. SALAMON in the Chair.

"On Purifying and Stabilising Gun-cotton." By ROBERT ROBERTSON, M.A., D.Sc.

This communication—published by permission of the War Office—deals with large scale experiments having for their object the best means of obtaining a pure and stable gun-cotton by a boiling process.

The investigations are described in two main divisions; first, those in which the effects of variations in the relative duration of the different boilings are examined, and, secondly, those in which alkaline treatments were employed.

For the elimination of impurities from the gun-cotton and the rapid attainment of a stable product, boiling in dilute acid at the beginning of the process is superior to an alkaline treatment which has the additional disadvantage

of tending towards an undue hydrolysis of the ester itself. It is brought out that the acid hydrolysis must not be unduly curtailed or elimination of the impurities will be rendered difficult.

The importance of retaining a certain degree of acidity in the first boiling is also shown, as is also the disadvantageous procedure of prolonged later boilings.

As a consequence of the foregoing the method of boiling was adopted, viz., a series of boilings characterised by long initial (acid) boilings followed by shorter (practical neutral) boilings.

"The Determination of Indigotin in Commercial Indigo and in Indigo-yielding Plants." By CYRIL BERGTHEIL and RICHARD VICTOR BRIGGS.

The authors have investigated the standard methods of estimating indigotin in commercial indigo. It is shown that all the methods dealt with are reliable when applied to pure indigotin, but that in application to commercial indigo the impurities present lead to errors; only those methods depending on the oxidation or reduction of solutions of sulphonated indigo are found to be applicable in this case. The methods which have been proposed for removing the undissolved impurities from solutions of sulphonated indigos are discussed, and it is shown that both that of Rawson (*Journ. Soc. Chem. Ind.*, 1899, xviii., 251) and that of Grossmann (*Journ. Soc. Chem. Ind.*, 1905, xxiv., 308) lead to precipitations of indigotin, and consequent errors in the results obtained. An alternative method of purifying the solution with freshly precipitated barium sulphate is described and shown to be free from the errors in the previous methods proposed.

The effect of the impurities which remain in solution is traced by making up indigos of known degrees of purity from pure indigotin and substances derived from the waste water from indigo manufacture, and is found to an error of from 1 to 2 per cent, for an indigo of average quality, in the methods investigated. The effect of indirubin is similarly traced. Oxidation with permanganate is found to supply a readier method of determining indigotin than reduction, methods depending on the latter principle being more troublesome and only applicable in conjunction with Grossmann's method of purification, which involves an error; they are, however, the most useful in dealing with indigos containing much indirubin.

A method for the determination of indigotin in indigo-yielding plants by precipitation from an extract with persulphuric acid has been described by Rawson ("Report on the Cultivation and Manufacture of Indigo," 1904), but it has been shown by Bergtheil (*Trans. Chem. Soc.*, 1904, lxxxv., 870) that the results obtained by its application do not coincide with those derived by fermentation with indigo enzyme. The authors have investigated the cause of this anomaly, and found it due to the employment of an excess of persulphuric acid by Rawson, and that, by suitably modifying the method, results may be obtained which agree with those obtained by fermentation.

"Recent Progress in the Cement Industry." By BERTRAM BLOUNT.

The author compares the condition of the cement industry in 1886 and at the present time, pointing out that at the former date somewhat crude methods of manufacture were in use, whereas now improved processes are in operation under scientific control. The world's production of Portland cement has increased from 2,500,000 tons to some 11,000,000 tons in the last 20 years, and the centre of the industry has shifted from Europe to the United States. The need for cheaper production to meet the competition of new centres of manufacture has stimulated the revision and improvement of the older methods of manufacture, and these have now been entirely remodelled; a great factor in the development which has occurred is the successful application of the rotatory process. A typical works of 1886 and a modern works with the latest form of plant are described and contrasted in respect to the mode of working and the cost and quality of the cement produced, mention

being made in the paper of the increased use of methods of mechanical conveyance and consequent diminution of labour.

The growing utilisation of cement for all structural purposes and for special methods of construction, such as the various systems of armoured concrete, is dealt with, and the present position of the industry considered, taking into account on the one hand the growing tendency of each locality to produce its own cement, and on the other, the much greater energy and technical skill of manufacturers. Cements other than Portland cement are discussed, and it is shown that, though the trade in them is large, and in some cases increasing, its importance relative to that of the Portland cement industry is diminishing. The utilisation of blast-furnace slag for making Portland cement, cement of the puzzuolana class, and Passow cement is referred to. Cement is made on the advantages of puzzuolana as an addition to Portland cement, and the preparation of white Portland cement is described.

The second part of the paper deals with improvements in controlling the quality of cement in the works and by the user which have been made during the last 20 years. Suggestions are made for further improvements in specifications. The outcome of the investigations which have taken place during the period under discussion on the chemistry of cement is described, the conclusions which appear to be best founded concerning both the composition of cement clinker and the reactions involved in the setting of cement being set forth.

A forecast is given of the lines on which the manufacture of Portland cement is likely to be evolved, and the advantages of some method by which the raw materials can be fused so as to avoid the present necessity of intimate grinding and mixing are indicated. The opinion is expressed that on its technical side the industry at the present date exhibits great and satisfactory advance from its status in 1886.

FARADAY SOCIETY.

Ordinary Meeting, June 12th, 1906.

Mr. W. MURRAY MORRISON in the Chair.

A PAPER ON "The Electrolytic Deposition of Zinc, using Rotating Electrodes," by Dr. T. SLATER PRICE and Mr. G. H. B. JUDGE was communicated by Dr. F. Mollwo PERKIN. (Will be inserted in full).

Dr. F. MOLLWO PERKIN described "A Simple Form of Rotating Cathode for Electro-chemical Analysis." (See p. 283).

Mr. S. BINNING and Dr. F. MOLLWO PERKIN read a paper on "The Electrolysis of Solutions of Thiocyanates in Pyridine and in Acetone."

On oxidation of thiocyanates with chlorine, persulphates, &c., a yellow colouring matter—canarine—is obtained. By electrolysis of aqueous acidified solutions of thiocyanates an apparently similar product, which was originally described in 1884 by Lurdow, is obtained. The authors consider that this substance is not identical with the canarine obtained by chemical means, because it shows certain reactions not given by the oxidation product. They find that in alkaline solutions no colouring matter is produced, but that cyanides are apparently formed. A difficulty met with in the electrolysis was the formation of the colouring matter on the anode surface, which caused a great resistance to the passage of the current. The difficulty was got over by using a lead cathode on which bristles had been fixed. This was rapidly rotated within a cylindrical platinum anode, the bristles cleaning the anode surface as the cathode rotated. With a current of 5 ampères (10 ampères per square decimetre) the E.M.F. was 5 volts.

Anhydrous ammonium thiocyanate readily dissolves in dry acetone and pyridine, in either case there being no difficulty in obtaining a 20 per cent solution. These solu-

tions readily conduct the electric current. In the case of the acetone solution with a current of 1.5 ampères (3 ampères per square decimetre) the E.M.F. required is 6.7 volts. With pyridine for the same current it is about 9 volts. In the case of the acetone solution a yellow amorphous powder separates out. With the pyridine solution the liquid becomes orange-red, but no precipitate is produced. On pouring this orange solution into a large excess of water an orange precipitate falls out. These two substances are certainly not identical with the canarine obtained by oxidation; at present the authors are unable to say whether the product obtained from acetone is the same as that produced from pyridine. It is found that when a lead anode is employed in the pyridine solution it goes into solution; lead thiocyanate is produced and metallic lead is deposited at the cathode.

NOTICES OF BOOKS.

The Elements of Chemical Engineering. By J. GROSSMANN, M.A. Ph.D., F.I.C. London: Charles Griffin and Co., Ltd. 1906.

THE scheme of this book, to which Sir William Ramsay contributes a preface, is as excellent as its working out, and every student of chemistry attending a technical course should obtain a copy. The object is to supply the link between the laboratory processes with which his training in pure chemistry should have made the student thoroughly familiar, and the corresponding manufacturing processes, which often present unexpected difficulties. For one thing, in the latter a new factor has to be taken into consideration, and has indeed become of paramount importance, and that is the cost of the process, including labour, which the student in the laboratory has been accustomed to neglect altogether. The author has endeavoured—and, we may add, with complete success—to make the transition between an operation on a small scale and its counterpart in the works, when tons have to be used instead of grammes, as gradual as possible. He takes the apparatus commonly employed in the laboratory, and by considering its limitations for manufacturing purposes, leads up to the construction and use of its equivalent in the works. Thus, for the beaker and evaporating dish, used for mixing, dissolving, evaporating, &c., the technical equivalents, the Thelen pan, iron or lead vessels, are substituted, and so on; constant appeals are made to the common sense of the student, who could hardly fail to be interested in the book, owing to the novel way in which the subject is presented and the author's particularly lucid style.

Systematic Inorganic Chemistry. By R. M. CAVEN, D.Sc. (London), and G. D. LANDER, D.Sc. (St. Andrews and London). London, Glasgow, and Dublin: Blackie and Son, Ltd. 1906.

THIS book is designed specially for the use of older students, and consequently the more elementary parts of the subject are omitted to make room for the further consideration of such aspects as are not dwelt upon in less advanced textbooks. The book thus gives an outline of the inorganic work of a degree student, and it will be found of considerable value, especially from a recapitulatory point of view. The authors possess the power of putting forward familiar facts in somewhat novel ways, which may be found of assistance to the memory, and the summaries of some theoretical subjects, such as the atomic and molecular theories, are both concise and complete. The elements are taken in groups according to the Periodic Law, and special attention is paid to the comparison of the properties and behaviour of the individual members of each group. The insertion of fuller references to original papers, to

which advanced students might be supposed to have access, would be an advantage from many points of view.

Joseph Priestley. By T. E. THORPE, F.R.S. London: J. M. Dent and Co. New York: E. P. Dulton and Co. 1906.

THIS life of Joseph Priestley will appeal to a large circle of readers, for it throws much light upon the intellectual activity of the eighteenth century, and incidentally also upon the methods of suppression adopted by our forefathers to stamp out views not approved by them. The famous Birmingham riots are dealt with very graphically, the account of an eye-witness, Miss Martha Russell, being quoted for this purpose. The book gives a detailed account of Priestley's scientific work, the value of which is discussed in a very critical spirit, the final result being to place it perhaps somewhat lower than is usually done. Long quotations are also made from his book "Experiments and Observations on Different Kinds of Air," and Dr. Thorpe gives a very interesting appreciation of it and summary of its contents.

The Dynamics of Living Matter. By JACQUES LOEB. New York: The Columbia University Press. London: Macmillan and Co., Ltd. 1906.

VOLUME VIII. of the excellent Biological Series issued by Columbia University is based upon the lectures delivered by the author before the University in the spring of 1902. It seems regrettable that the book could not have been published rather sooner after the course of lectures, but the subject has been brought down to a more recent date and treated considerably more fully, and many who remember the interest the lectures awakened in the first instance will be glad of an opportunity of reading them in this form. The chapters on the general chemistry of life phenomena, the physical constitution of living matter, and the effects of heat and radiant energy on living matter will be found by no means unduly difficult of comprehension by those whose biological knowledge is slight, and the general character of the book is exceedingly stimulating, for it contains full accounts of the author's own important investigations, and while his views are unmistakably discernible in every page, it is written in a temperate spirit.

Notes on Electrochemistry. By F. G. WIECHMANN, Ph.D. New York: McGraw Publishing Company. 1906.

THIS small book is intended to give a general survey of electrochemistry to be used by students as an introduction to larger works, and also by chemists interested in the applications of electricity. Its use may possibly break the way for the beginner, but no student should attempt to cope with the problems and difficulties of electrochemistry until he has thoroughly mastered the elementary principles both of chemistry and mathematics. Hence, it should be superfluous in a book of this kind to give definitions of chemical equivalents for instance, or explanations of the meaning of 10^6 and 10^{-6} , and the fact that these and similar explanations are included leads us to regard the book as meant merely to provide a short cut to a knowledge of electrochemistry for the student who has not had the preliminary training which is absolutely indispensable for a thorough understanding of the subject. As for its contents, the book gives an introduction of definitions and explanations of the terms used, also an outline of the electrolytic theory, and a sketch of some of the applications of electrochemistry in technology. These are grouped as direct and indirect processes, the first including electro-deposition for solutions, while the second group comprises electro-depositions from fused electrolytes, and all electro-thermic processes. The difficulty of giving in a space of some forty pages an anything like adequate idea of most of the common applications no doubt accounts for the slightness of the treatment, which is such as to give in some cases a

very imperfect and even erroneous view of the actual processes.

A Text-book of Assaying. By C. and J. J. BERINGER. Revised by J. J. BERINGER. Tenth Edition. London: Charles Griffin and Co., Ltd. 1906.

THIS book has been universally recognised as one of the best of its kind and size, and it is so well known that it is hardly necessary to point out its special merits. For the preparation of the tenth edition the text has been thoroughly revised, and the chapter on the wet methods of assaying for lead has been entirely re-written.

Peace and War. By CH. RICHET. Translated by MARIAN EDWARDS. London: J. M. Dent and Co. 1906.

THIS book, which is translated from the French, deals with the question whether, in view of the psychological nature of mankind, a state of unbroken peace is possible, and, furthermore, desirable. The author first discusses the desirability and then the possibility of the abolition of war, which a moment's reflection will show is hardly the most convincing method of considering the subject, and two-thirds of the book is devoted to arguments with which the majority of readers will agree, showing that war is an evil, although it may be pointed out that the deduction based upon "the survival of the unfit" is of more force against compulsory than voluntary military service. The last part of the book contains some sensible, though perhaps not original, remarks on education on pacific principles as a means of leading to the abolition of war and its attendant evils.

Les Industries de la Conservation des Aliments. ("The Industries Connected with the Preservation of Foods"). By X. ROCQUES. Paris: Gauthier-Villars. 1906.

THERE seems to be no limit to the issue of books on the subject of preservatives in food, but the one now under review is a not unwelcome addition to their number; it takes a very moderate view of the vexed question, and, moreover, gives a complete account of the various physical methods employed to hinder putrefaction. As regards the addition of antiseptics, only a small part of the book is devoted to its consideration; the author believes that the opinion of the majority of experts is that such additions are harmful to health, and ought to be forbidden by law, and with this view he concurs, after discussing the nature and use of the most common preservatives. A special chapter deals with the preservation of eggs, which is of great importance in France, where the poultry-keepers are not, as a rule, successful in obtaining new laid eggs in winter. The greater part of the book is occupied with the description of the apparatus and methods used to preserve food-stuffs by the application of high or low temperatures, or by desiccation, of which subjects M. Rocques shows that he is well qualified to write authoritatively.

The Dipping Refractometer. Third Edition. Jena: Carl Zeiss. 1905.

THE method of examining fats and oils with the refractometer is being continually more used by analytical chemists, possessing as it does the advantages of being quick, accurate, and simple. With the Dipping Refractometer, the use of which is clearly and fully described in this pamphlet, it is claimed that a careful worker can get results accurate to ± 3.7 units in the fifth decimal place of n_D . The method of measuring the refraction of light in a liquid by immersing the prism, after a little practice with this instrument, is as simple as taking its temperature with a thermometer, and the border-line appears much sharper than in other refractometers, so that the degree of accuracy is considerably greater. In combination with the heating spiral and water pressure regulator, the Dipping Refractometer

meter can be used to determine the refractive index of beer, albumen in blood, cane-sugar, and all kinds of salts in solution, and considering the wide applicability of the method, the price of the instrument and its accessories is by no means high.

CORRESPONDENCE.

PROPOSED SOCIETY OF ALCOHOL RESEARCH.

To the Editor of the Chemical News.

SIR,—I take the liberty of calling your attention to a letter which appears in the Correspondence columns of the current issue of *The Autocar* under the above title, in the hope that you may see your way to further the proposal in your columns, seeing that the subject is vital to the motor and agricultural industries, and that we look to chemists to solve the difficulty.—I am, &c.,

RADFORD COOKE.

19, Hanover Square, London, W.,
June 30, 1906.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 23, June 5, 1906.

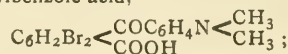
Researches on Rubidium, Cæsium, and Lithium.—M. de Forcrand.—The author finds the heat of solution of hydrated rubidium hydrate, $\text{RbOH} + \text{H}_2\text{O}$, to be 3.702 cal. at $+15^\circ$. He deduces this number from a number of concordant experiments made at about $+20^\circ$. The heat of solution of pure rubidium hydrate, RbOH , calculated in the same manner, is 14.264 cal. at 15° . Cæsium has a hydrate, $\text{CsOH} + \text{H}_2\text{O}$, which is obtained commercially. The heat of solution at 15° is 16.423 cal., whilst that of the hydrate, $\text{CsOH} + \text{H}_2\text{O}$, is 4.317 cal. at 15° , from which may be deduced $\text{CsOH sol.} + \text{H}_2\text{O liq.} = \text{CsOH} + \text{H}_2\text{O sol.} \dots + 12.106 \text{ cal.}$ The slow evaporation of very concentrated solutions of cæsium in the cold leaves fine needles of a secondary hydrate, probably of formula $\text{CsOH} + 3 \text{ or } 4 \text{ H}_2\text{O}$, which melts about 25° . Lithium hydrate, $\text{LiOH} + \text{H}_2\text{O}$, when dissolved absorbs 0.720 cal. at 18° , whilst LiOH absorbs $+4.477 \text{ cal.}$, from which may be deduced $\text{LiOH sol.} + \text{H}_2\text{O liq.} = \text{LiOH} + \text{H}_2\text{O sol.} + 3.757 \text{ cal.}$

Action of Silicon Chloride on Nickel.—Em. Vigouroux.—During an investigation of the action of silicon chloride on nickel, the author observes two limits of siliciuration. The lower limit corresponding to Ni_4Si , a substance hitherto unknown, but now perfectly defined, its action on a magnet proving it to contain no free nickel. The higher limit, giving the body Ni_2Si , a substance well known. It is not impossible that higher temperatures may be capable of inducing the formation of more strongly siliciuretted compounds.

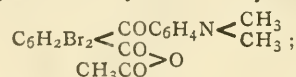
Decomposition of Copper Sulphate by Methylic Alcohol.—V. Auger.—The author finds that sulphate of copper is decomposed by methylic alcohol, both in the cold and when hot, and whether anhydrous or hydrated, and his explanation of the phenomenon is that the methylic sulphuric ether-acid is formed. The sulphate of copper in solution being always slightly dissociated, the formation of this acid-ether disturbs the equilibrium $\text{SO}_3 \rightleftharpoons \text{basic salt} + \text{sulphate}$, and causes the formation of a new proportion of the latter. Ethylic alcohol also gives a basic salt, but in extremely small proportion. It is

thus seen that methylic alcohol, the first term of the fatty alcohols, always shows a much greater activity than the superior homologues.

Dibromo-dimethyl- and Diethylamidobenzoylbenzoic Acids and their Derivatives.—E. Séverin.—When phthalic anhydride is condensed with the dialcyl-anilines in presence of AlCl_3 , dialcylamidobenzoylbenzoic acids are obtained. The author's researches were carried out upon dibromophthalic acid, which he considers as para-derivatives 1.2.3.6. The anhydride of this acid is used to prepare the following bodies:—Dibromodimethylamidobenzoylbenzoic acid,—



dibromoacetylamidobenzoylbenzoic anhydride,—



also the ethylic ether, methylic ether, nitroso-derivative, and a few other compounds.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., His Grace the Duke of Northumberland, K.G., F.R.S., President, in the Chair. The Hon. Arthur Stanley, M.V.O., M.P., Dr. T. P. Hyslop, and Dr. J. G. McKendrick were elected Members. The special thanks of the members were returned to the Rt. Hon. Lord Sanderson, G.C.B., K.C.M.G., for his donation of five guineas to the fund for the Promotion of Experimental Research at Low Temperatures.

Compounds of Mercuric Iodide and Free Mono-methylamine.—Maurice François.—If $\text{HgI}_2 \cdot \text{CH}_3\text{N}$ is the possible compound of mercuric iodide and methylamine containing the least quantity of methylamine, and if h is the tension of dissociation, it is evident that the mercuric iodide ought only to absorb the methylamine in proportion as the tension is greater than the dissociation tension h . This would lead to the compound $\text{HgI}_2(\text{CH}_3\text{N})_2$, the one immediately below, without allowing a more complete decomposition. This is theoretically true in the absence of air, and is practically realised even in presence of air. The compound $\text{HgI}_2 \cdot \text{CH}_3\text{N}$ is yellowish white; it only yields red mercuric iodide with difficulty and after long exposure to air. It can be prepared when a solution of free methylamine is poured into an excess of potassium iodide solution saturated with mercuric iodide; it is then crystalline.—*Comptes Rendus*, cxlii., No. 22.

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Based on Remarks made in the Presidential Address to the British Association at Bristol in 1898.

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By SIR WILLIAM CROOKES, F.R.S.

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THE CHEMICAL NEWS.

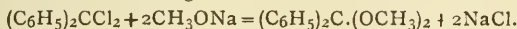
VOL. XCIV., No. 2433.

ON THE CONDENSATION PRODUCTS OF α -NAPHTHOL AND BENZOPHENONE CHLORIDE.

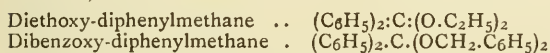
By ALBERT G. SHRIMPTON, B.Sc.

THE series of condensation products of benzophenone chloride and benzal chloride with the alcohols, phenols, &c., was commenced by Wicke (*Annalen*, 1857, cii., 356). He examined the action of sodium methoxide and its homologues on benzal chloride, *e.g.*,—

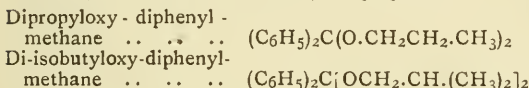
$C_6H_5 \cdot CHCl_2 + 2CH_3ONa = C_6H_5 \cdot CH(OCH_3)_2 + 2NaCl$,
in which the compound dimethoxy-benzylidene was formed. Dr. J. E. Mackenzie continued the work (*Trans. Chem. Soc.*, 1896, lxi., 985), using benzophenone chloride instead of benzal chloride, *e.g.*,—



By this process he prepared dimethoxy-diphenylmethane, also—



Later (*Ibid.*, 1901, lxxix., 1204), he prepared:—



He also prepared 4:4'-dihydroxy-tetraphenylmethane,—
 $(C_6H_5)_2C(C_6H_4OH)_2$,

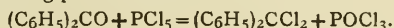
by using sodium phenoxide. It will be noticed that in the formation of the previous products the reaction was directed to a great extent by the presence of sodium in the hydroxyl group. But in the case of the last mentioned substance preference is shown for the benzene nucleus:—



No phenoxy compound could be isolated. (Another peculiarity is shown by this substance crystallising with two molecules of ether). It can also be prepared by the direct action of benzophenone chloride on phenol.

Hence it was desirable to continue the study by examining the action of benzophenone chloride on α -naphthol.

For this work benzophenone chloride was prepared according to the method of Kekulé and Franchimont. Thirty grms. of benzophenone and 35 grms. of phosphorus pentachloride (in molecular proportions) were placed in a round-bottom flask connected to a reflux air condenser, which terminated in a calcium chloride guard-tube. On careful heating in an oil-bath, the benzophenone began to boil at 140—150° C., when the phosphorus pentachloride melted. The temperature was gradually raised to 207°, when the reaction proceeded fairly vigorously, and was maintained at this temperature for four hours and a-half. The resulting products were brownish.



The products were separated by distillation under reduced pressure. 20.55 grms. of phosphorus oxychloride distilled over at 45.5—46° C. under 53 m.m. pressure. The residue was heated to 100° for a few minutes to ensure the com-

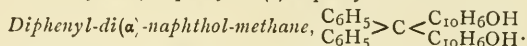
plete separation of the oxychloride. Benzophenone chloride began to distil over at 198° C.

198° C. under pressure of 38 m.m.	..	16.2 grms.
200—204° C. " " "	43 "	.. 17.5 "
+ 204° C. " " "	43 "	.. 3.46 "

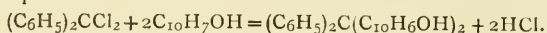
In all 36.81 grms. of benzophenone chloride were collected, being 94.4 per cent of the theoretical.

In distilling this substance under reduced pressure great trouble was experienced by the liquid bumping over. This was remedied by bending the exit tube of the Wurtz flask, first upwards at about 30° to the neck, and again downwards. Also benzophenone chloride readily attacks rubber, so it is necessary to push the exit tube of the flask as far as possible through the rubber cork of the condenser.

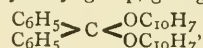
Dihydroxy-diphenyl-di(α)-naphthyl-methane.



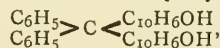
—This substance was formed by the condensation of α -naphthol with benzophenone chloride according to the equation:—



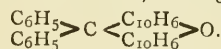
It is possible for the reaction to take place in three ways, excluding all the subsidiary actions:—The condensation taking place between the chlorine and the hydrogen of the hydroxyl group, giving rise to—



with the hydrogen atom of the naphthyl nucleus,—



or, lastly, a further action could take place by one molecule of water splitting off from the two hydroxyl groups (especially if the two hydroxyl groups were stereo-isomerically near to one another) forming—



29.7 grms. of benzophenone chloride were mixed with 38.1 grms. of α -naphthol in a round bottomed flask fitted with a reflux air condenser terminating in a calcium chloride guard tube. The flask was heated on an oil-bath. At 68° the mass began to swell considerably, to char, and give off copious fumes of hydrochloric acid. The temperature was gradually raised to 200° for fifteen hours until the hydrochloric acid ceased to come off. During the operation a beautiful violet coloration was often observed, at first on the mixing of the substances and afterwards near the neck of the flask. The α -naphthol frequently distilled up into the condenser, often having the appearance of drops of water. The flask was disconnected and weighed. The loss in weight amounted to 9.0 grms. The theoretical loss due to the evolution of two molecules of hydrochloric acid is 9.12 grms. The residue was a very dark brown solid tar. At first a separation under reduced pressure was tried, but only the α -naphthol unacted upon distilled over. Weight of crude substance was 49.12 grms., which is equal to 87 per cent of the theoretical yield.

To extract this substance from the tar many methods had to be adopted. None were very successful, but the following gave the best results:—

1. The tar was removed from the flask with boiling benzol. On cooling, this yielded a fair crop of pinkish, sandy, microscopic crystals, but beyond this the use of benzoyl is not efficacious as it only deposits a very sticky unyielding tar.

2. A dilute solution of the substance in benzol, or better in chloroform, can be precipitated by shaking up with petroleum ether in the cold and quickly filtering off. The solution must be dilute, and excess of petroleum ether added, otherwise the tar separates out again.

3. The tar can also be shaken up or stirred with a solution of sodium hydrate. A fine madder-brown solution

having a blue fluorescence is obtained. This is filtered off from the rest of the tar (or decanted off). On the addition of hydrochloric acid the substance is precipitated as a pinkish white powder, which rapidly turns brown on standing.

4. Probably the best method is to place a little concentrated solution of the substance in a conical flask. To this is added an excess of alcohol, well shaken, and filtered directly.

(In another experiment a first extraction was made with boiling ether. When cold petroleum ether was added, a slight precipitate was obtained, which when dry had a beautiful violet colour. But it showed no definite melting-point, apparently decomposing from 90° upwards). The precipitates were re-crystallised several times from chloroform, but up to now no satisfactory yield has been obtained.

Analysis gave the following figures:—

0.1053 grm. substance gave 0.3424 CO_2 , 0.0548 H_2O .
C = 88.57 per cent, H = 5.77 per cent. (Preliminary).
0.1408 grm. substance gave 0.4504 CO_2 , 0.0650 H_2O .
C = 87.24 per cent, H = 5.13 per cent.

$\text{C}_{33}\text{H}_{24}\text{O}_2$ requires C = 87.61, H = 5.31.
 $\text{C}_{33}\text{H}_{22}\text{O}$ requires C = 91.24, H = 5.07.

This shows the substance to be dihydroxy-diphenyl-di- α -naphthyl methane. This is confirmed by a Raoult's cryoscopic determination by the depression of the freezing-point (using a Bechmann's apparatus), which gave for its molecular weight 465.

$\text{C}_{33}\text{H}_{24}\text{O}_2$ requires 452. $\text{C}_{33}\text{H}_{22}\text{O}$ requires 434.

This is further confirmed by the acetyl derivative, and also by the formation of the madder-brown compound with sodium hydrate.

Diphenyl di- α -naphthol methane is a white substance consisting of microscopic crystals, melting-point = 208.2 — 209.2° C. (with 210° exposed). It begins to darken at 204° , changing to grey, reddish brown, and finally melting to a brownish viscid liquid. When impure it soon becomes pinkish on exposure to air, and finally becomes a deep brown. This is probably due to oxidation. It is soluble in benzene, carbon disulphide, ether, acetone, and chloroform, less soluble in alcohol and petroleum ether. It dissolves in an aqueous solution of sodium hydrate, giving a madder-brown solution which shows a blue fluorescence. On the addition of mineral acids the substance is thrown down.

Attempt to prepare a Diacetyl Derivative of Diphenyl-Di- α -naphthol Methane.

1.1 grm. of diphenyl-di- α -naphthol methane were mixed with 1.3 grms. of freshly fused sodium acetate and 4.8 grms. of acetic anhydride. The mixture was heated on a water-bath under a reflux condenser for four hours. By this time the product had become pasty. On cooling, it showed a brownish white crystalline structure. Water was added to the cooled mass and made just alkaline with sodium hydrate. The solid residue was filtered off, and thoroughly washed with water until there was no further smell of acetic acid. The substance was re-crystallised several times from acetone. The crystals consisted of small silky white needles and plates, which showed a definite melting-point of 202° C. They melted to a colourless liquid which showed no signs of colouring until the temperature of 208° was reached.

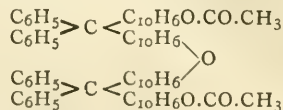
The quantitative results were disappointing, and unfortunately there was not enough substance to repeat them.

0.1453 grm. of substance gave CO_2 = 0.4617 and H_2O = 0.0707 grm. C = 86.66 per cent, H = 5.41 per cent.

A diacetyl derivative requires C = 82.84 per cent, H = 5.22 per cent.

A monacetyl derivative requires C = 85.02 per cent, H = 5.26 per cent.

But a condensation between two monacetyl derivatives, such as—



requires C = 86.56 per cent, H = 5.15 per cent.

But a Raoult's cryoscopic determination by the depression of the freezing-point only gave 244.15 for the molecular weight.

A Second Condensation Product of Benzophenone Chloride with α -Naphthol.

As the method adopted for the preparation of diphenyl-di-(α)-naphthol methane had resulted in such a large quantity of a troublesome tar, it was thought expedient to try a method in which the action could be more under control. For this purpose 21.7 grms. of benzophenone chloride were placed in a capacious flask, and 500 c.c. of petroleum ether, previously dried over metallic sodium, added. The flask was attached to a reflux Liebig's condenser terminating in a calcium chloride guard tube. About 0.5 grm. of α -naphthol were added. This at first turned the liquid a beautiful blue. On heating the flask on a water-bath the action commenced at 70° C., when hydrochloric fumes were evolved. The action slackened off after fifteen minutes. This operation was repeated by adding about 0.5 grm. of α -naphthol at a time until the whole of 26.5 grms. (theoretically required) had been added. The solution became yellow and deposited a little tar. But I believe this can be prevented by having pure ingredients and preventing the action from becoming too rapid. After a time the action commenced at 62° and became vigorous at 66 — 68° . It took thirty-six hours for the action to be completed.

The supernatant liquid was filtered off hot. On the addition of a few drops of sulphuric ether the liquid was clarified, and immediately began to deposit yellow crystals as a flocculent mass. The presence of tar prevents crystallisation. The residue in the flask was repeatedly washed with small quantities of boiling sulphuric ether, which dissolved out the tar, leaving a fairly pure product of a yellow colour behind. This was re-crystallised from acetone. The yield was far greater than that of the previous method.

This substance is soluble in benzol, ethyl alcohol, and acetone, less soluble in petroleum ether and sulphuric ether, fairly soluble in carbon disulphide and carbon tetrachloride. It consists of fine yellow microscopic crystals. They are stout prisms having an angle of 74 — 78° , and are isotropic.

The melting-point was sharp. Melting-point, 180.5 — 181° C. Up to now no satisfactory numbers have been obtained for this compound. The endeavour to obtain an acetyl derivative gave a negative result. This substance also shows good dyeing properties.

Action of Sulphuric Acid on Platinum.—L. Quennessen.—The author makes a number of researches on the action of pure platinum on sulphuric acid of different degrees of concentration and also *in vacuo*, the intervention of oxygen having been clearly proved by former experiments. He shows that when commercial acid is used, it is clearly the oxygen of the air which intervenes as an oxidising agent, whilst with sulphuric acid in the absence of free oxygen it is the sulphuric anhydride in solution in the sulphuric acid which gives the necessary oxygen for oxidation owing to a phenomenon of the same kind as that which causes the preparation of sulphurous anhydride with some of the common metals. The mechanism can be understood if Dittmar's work on the dissociation of SO_4H_2 into SO_3 and water in very concentrated sulphuric acid be referred to.—*Comptes Rendus*, cxlii., No. 24.

NOTES OF A COURSE OF LECTURES ON THE
OLD AND NEW CHEMISTRY.*

I. EXTRACTS FROM DIFFERENT AUTHORS RELATING TO
THE OLD CHEMISTRY.

By Prof. Sir JAMES DEWAR, F.R.S., &c.

(Continued from p. 5).

Works of Alchemical Adepts.—Sir Humphry Davy, vol. viii.

"WITH respect to the views of the adepts of the alchemists who pretended to be in possession of the philosopher's stone, there cannot be two opinions.

"Nothing can be stronger or more just than what Lemery said of these men, 'That they professed an art without principle, the beginning of which was deceit, the progress of which was falsehood, and the end beggary.' There were, however, enlightened alchemists—men who modestly asserted that their means were inadequate to produce effects which they conceived to take place in the external world, who, considering the metals as generated beneath the surface of the earth by unknown operations, directed their views towards the discovery of these processes, and had for their highest object the construction of a laboratory in art correspondent to the great laboratory in nature.

"In this point of view, Helmont was an alchemist, Becher was an alchemist, Stahl was an alchemist.

"These men, the fathers of philosophical chemistry, had witnessed the most extraordinary effects of the apparent conversion of metals into each other, even in artificial processes.

"It required considerable labour to prove that in the precipitation of copper by iron it was not an actual transmutation, which certainly is the obvious explanation. There is no physical impossibility in the idea. It appeared even more probable than some facts which have been since discovered.

"Even in these times of a more exalted science, after a series of connected discoveries, we have no right to say that what Stahl suspected—the generation of gold in nature—does not take place. We, it is true, have never seen it composed or decomposed; but our works are in moments, those of nature in ages; and but very lately there were many other bodies in the same case, which are now known not to be elementary."

The Object of Alchemy and Attainments of the Alchemists.
—Draper.

"As there are veins of water in the earth and apertures through which the air can gain access, an analogy was inferred between its structure and that of an animal, leading to an inference of a similarity of functions. From this came the theory of the developments of metals in its womb under the influence of the planets. Already, however, in the doctrine of the transmutation of metals, it was perceived that to Nature the lapse of time is nothing—to man it is everything. To Nature when she is transmuting a worthless into a better metal, what signifies a thousand years? The aim of the cultivator of the sacred art should be to shorten the natural term; and since we observe the influence of heat in hastening the ripening of fruits, may we not reasonably expect that duly regulated degrees of fire will answer the purpose? by an exposure of base materials in the furnace for a proper season may we not anticipate the wished-for event? The Emperor Caligula, who had formerly tried to make gold from orpiment by the force of fire, was only one of a thousand adepts. Some trusted to the addition of a material substance in aiding the fire to purge away the dross of the base body submitted to it. From this arose the doctrine of the powder of projection and the philosopher's stone.

"This doctrine of the possibility of transmuting things

into forms essentially different steadily made its way, leading in the material direction to alchemy, the art of making gold and silver out of baser metals, and in theology, to transubstantiation: transmutation and transubstantiation were twin sisters destined for a world-wide celebrity. . . .

"While thus the Arabs joined in the pursuit of alchemy, their medical tendencies led them simultaneously to cultivate another ancient delusion, the discovery of a universal panacea or elixir which should cure all diseases and prolong life for ever. The mystical experimenters for centuries had been ransacking all nature from the yellow flowers which are sacred to the sun, and gold, his emblem and representative on earth, down to the vilest excrements of the human body. As to gold, there had gathered round that metal many fictitious excellences in addition to its real values; it was believed that in some preparation of it would be found the elixir vitæ. This was the explanation of the unwearied attempts at making potable gold, for it was universally thought that if that metal could be obtained in a dissolved state, it would constitute the long-sought panacea. Nor did it seem impossible so to increase the power of water as to impart to it new virtues, and thereby enable it to accomplish the desired solution. Were there not natural waters of very different properties? Were there not some that could fortify the memory, others destroy it; some reinforce the spirits, some impart dulness; and some, which were highly prized, that could secure a return of love? . . . Zosimus the Panopolitan had described in former times the operation of distillation, by which water might be purified; the Arabs called the apparatus for conducting that experiment an alembic. . . .

"The practical Arabs had not long been engaged in these fascinating but wild pursuits, when results of very great importance began to appear. In a scientific point of view, the discovery of the strong acids laid the true foundation of chemistry; in a political point of view the invention of gunpowder revolutionised the world.

"There were several explosive mixtures, automatic fire, liquid Greek fire, the knowledge of which was kept at Constantinople as a state secret. Of gunpowder, Marcus Græcus, whose date is probably to be referred to the close of the eighth century, gives the composition explicitly. It would appear that fireworks preceded fire-arms, as we have the undoubted description of a rocket by the same writer. To this author we are indebted for receipts for making the skin incombustible so that we may handle fire without being burnt. These doubtless were received as explanations of the legends of the time which related how miracle-workers had washed their hands in melted copper, and sat at their ease in burning straw. The definition of alchemy by some of the old Saracen chemists is very striking: the science of the balance, the science of weight, the science of combustion.

"To one of these cultivators of alchemy, Djafar, who lived toward the end of the eighth century, our attention may for a moment be drawn. He is the first to describe nitric acid and aqua regia. Before him no stronger acid was known than concentrated vinegar. (Cleopatra and the pearl dissolved in vinegar).

"His doctrine respecting the nature of metals, though erroneous, was not without a scientific value. A metal he considers to be a compound of sulphur, mercury, and arsenic, and hence he infers that transmutation is possible by varying the proportions of those ingredients. He knows that a metal, when calcined, increases in weight. . . . He describes the operation of distillation, sublimation, filtration, various chemical apparatus, water-baths, sand-baths, cupels of bone earth, of the use of which he gives a singularly clear description. A chemist reads with interest Djafar's antique method of obtaining nitric acid by distilling in a retort Cyprus vitriol, alum, and saltpetre. He sets forth its corrosive power, and shows how it may be made to dissolve even gold itself, by adding a portion of sal-ammoniac. Djafar may thus be considered as having solved the grand alchemical problem of obtaining gold in a potable state; and there can be no doubt but many trials

* Delivered at the Royal Institution, May 19th, 1906.

were made on the influence of this solution on the animal system.

"With Djafar may be mentioned Rhazes, born A.D. 860, physician in chief to the great hospital at Bagdad. To him is due the first description of the preparation and properties of sulphuric acid. He obtained it as the Nordhausen variety is still made, by the distillation of dried green vitriol. To him also are due the first indications of the preparation of absolute alcohol, by distilling spirits of wine from quicklime. As a curious discovery made by the Saracens may be mentioned the experiment of Achilid Bechil, who, by distilling together the extract of urine, clay, lime, and powdered charcoal, obtained an artificial carbuncle, which shone in the dark 'like a good moon.' This was phosphorus. . . .

"The pursuit of the elixir made a well-marked impression upon Arab experimental science, confirming it in its medical application. At the foundation of this application lay the principle that it is possible to relieve the diseases of the human body by purely material means. As the science advanced it gradually shook off its feticisms, the spiritual receding into insignificance, the material coming into bolder relief. Not, however, without great difficulty was a way forced for the great doctrine that the influence of substances on the constitution of man is altogether of a material kind, and not at all due to any indwelling or animating spirit; that it is of no kind of use to practise incantations over drugs, or to repeat prayers over the mortar in which medicines are being compounded, since the effect will be the same whether such has been done or not; and there is no kind of efficacy in amulets, no virtue in charms."

The Sceptical Chymist, or Chymico-Physical Doubts and Paradoxes touching the Experiments whereby vulgar Spagyrist are wont to endeavour to evince their Salt, Sulphur, and Mercury, to be the true Principles of Things. (Oxford, 1661).

"To be short, as the difference of bodies may depend merely upon that of the schemes, whereinto their common matter is put; so the seeds of things, the fire and the other agents are able to alter the minute parts of a body (either by breaking them into smaller ones of differing shapes, or by uniting together these fragments with the unbroken corpuscles, or such corpuscles among themselves) and the same agents, partly by altering the shape or bigness of the constituent corpuscles of a body, partly by driving away some of them, partly by blending others with them, and partly by some new manner of connecting them, may give the whole portion of matter a new texture of its minute parts, and thereby make it deserve a new and distinct name. So that, according as the small parts of matter recede from each other, or work upon each other, or are connected together after this or that determinate manner, a body of this or that denomination is produced, as some other body happens thereby to be altered or destroyed.

"Since then, those things, which chymists produce by the help of the fire, are but inanimate bodies; since such fruits of the chymist's skill differ from one another but in so few qualities, that we see plainly, that by fire, and other agents we can employ, we can easily enough work as great alterations upon matter, as those that are requisite to change one of these chymical productions into another; since the same portion of matter may, without being compounded with any extraneous body, or at least, element, be made to put on such a variety of forms, and consequently to be (successively) turned into so many differing bodies; and since the matter, clothed with so many differing forms, was originally but water, and that in its passage through so many transformations, it was never reduced into any of those substances, which are reputed to be the principles or elements of mixt bodies, except the violence of the fire, which itself divides not bodies into perfectly simple or elementary substances, but into new compounds; since,

I say, these things are so, I see not, why we must needs believe, that there are any primogeneal and simple bodies, of which, as of pre-existent elements, nature is obliged to compound all others. Nor do I see, why we may not conceive that she may produce the bodies accounted mixt out of one another, by variously altering and contriving their minute parts, without resolving the matter into any such simple or homogeneous substances, as are pretended. Neither, to dispart, do I see, why it should be counted absurd to think, that when a body is resolved by the fire into its supposed simple ingredients, those substances, are not true and proper elements, but rather were, as it were, accidentally produced by the fire, which by dissipating a body into minute parts does, if those parts be shut up in close vessels, for the most part necessarily bring them to associate themselves after another manner than before, and so bring them into bodies of such different consistences, as the former texture of the body and concurrent circumstances make such disbanded particles apt to constitute; as experience shows us (and I have both noted it, and proved it already) that as there are some concretes whose parts, when dissipated by fire, are fitted to be put into such schemes of matter as we call oil, and salt, and spirit; so there are others, such as are especially the greatest part of the minerals, whose corpuscles being of another size or figure, or perhaps contrived another way, will not in the fire yield bodies of the like consistences, but rather others of differing textures; not to mention, that from gold and some other bodies, we see not, that the fire separates any distinct substances at all; nor that even those similar parts of bodies, which the chymists obtain by the fire, are the elements, whose names they bear, but compound bodies, upon which, for their resemblance to them in consistence, or some other obvious quality, chymists have been pleased to bestow such appellations."

Sir Isaac Newton as an Alchemist.—Brewster.

"During the four years, from 1683 to 1687, the period in which the "Principia" was composed, he never abandoned his chemical experiments.

"Dr. H. Newton, who was his amanuensis during that time, tells us that during six weeks in spring and autumn, he was so constantly occupied in his laboratory that he was scarcely out of it either night or day, that the fire in it was almost always burning, that it was well furnished with chemical materials and apparatus, and that the transmuting of metals was his chief design.

"The alchemy of Boyle, Newton, and Locke cannot be thus characterised. The ambition neither of wealth nor of praise prompted their studies, and we may safely say that a love of truth alone, a desire to make new discoveries in chemistry, and a wish to test the extraordinary pretensions of their predecessors and their contemporaries, were the only motives by which they were actuated. In so far as Newton's inquiries were limited to the transmutation and multiplication of metals, and even to the discovery of the universal tincture, we may find some apology for his researches; but we cannot understand how a mind of such power, and so nobly occupied with the abstractions of geometry, and the study of the material world, could stoop to be even the copyist of the most contemptible alchemical poetry, and the annotator of a work, the obvious production of a fool and a knave; such, however, was the taste of the century in which Newton lived; and when we denounce the mental epidemics of a past age, we may find some palliation of them in those of our own times.

"Leibnitz, his great rival, was also an alchemist. In his early life he was secretary to the Society of Rosicrucians at Nuremberg—a secret association which practised alchemy, and which existed in several of the larger towns in Germany. Leibnitz, however, soon renounced his faith in the mystic art, and, there is reason to believe, from one of Newton's letters to Locke, that he also had learned to have but little confidence even in the humbler department of the multiplication of metals."

Explanation of Chemical Action and Elective Attraction.—
Sir Isaac Newton.

"Have not the small particles of bodies certain powers, virtues, or forces, by which they act at a distance, not only upon the rays of light for reflecting, refracting, and inflecting, but also upon one another, for producing a great part of the phenomena of nature? For it is well known that bodies act one upon another by the attractions of gravity, magnetism, and electricity; and these instances show the tenor and course of Nature, and make it not improbable but that there may be more attractive powers than these. For Nature is very consonant and conformable to herself. How these attractions may be performed I do not here consider. What I call attraction may be performed by impulse, or by some other means unknown to me. I use that word here to signify only in general any force by which bodies tend towards one another, whatsoever be the cause. For we must learn from the phenomena of Nature, what bodies attract one another, and what are the laws and properties of the attraction, before we inquire the cause by which the attraction is performed. The attractions of gravity, magnetism, and electricity, reach to very sensible distances, and so have been observed by vulgar eyes; and there may be others which reach to so small distances as hitherto to escape observation; and perhaps electrical attraction may reach to such small distances, even without being excited by friction.

"The parts of the homogeneous hard bodies which fully touch one another stick together very strongly; and for explaining how this may be, some have invented hooked atoms, and others tell us that bodies are glued together by Rest, that is, by an occult quality, or rather by nothing; and others that they stick together by conspiring motions, that is, by relative rest amongst themselves. I had rather infer from the cohesion that their particles attract one another by some force which in immediate contact is exceeding strong, at small distances performs the chemical operations above mentioned, and reaches not far from the particles with any sensible effect.

"Now the above-mentioned notions are so great and violent, as to show that in fermentations the particles of bodies which almost rest are put into new motions by a very potent principle, which acts upon them only when they approach one another, and causes them to meet and clash with great violence, and grow not with the motion, and dash one another into pieces, and vanish into air, and vapour, and flame."

Dr. Watson, Professor of Chemistry at Cambridge, 1764,
on Phlogiston.

"Notwithstanding all that perhaps can be said upon this subject, I am sensible the reader will still be ready to ask, *What is phlogiston?* You do not surely expect that chemistry should be able to present you with a handful of phlogiston, separated from an inflammable body; you may just as reasonably demand a handful of magnetism, gravity, or electricity to be extracted from a magnetic, weighty, or electric body. There are powers in nature which cannot otherwise become the objects of sense, than by the effects they produce; and of this kind is phlogiston. But the following experiments will tend to render this perplexed subject somewhat more clear.

"If you take a piece of sulphur and set it on fire, it will burn entirely away, without leaving any ashes or yielding any soot. During the burning of the sulphur, a copious vapour, powerfully affecting the organs of sight and smell, is dispersed. Means have been invented for collecting this vapour, and it is found to be a very strong acid. The acid thus procured from the burning of sulphur, is incapable of being either burned by itself, or of contributing towards the support of fire in other bodies; the sulphur, from which it was procured was capable of both; there is a remarkable difference, then, between the acid procured from the sulphur, and the sulphur itself. The acid cannot be the

only constituent part of sulphur; it is evident that something else must have entered into its composition, by which it was rendered capable of combustion. This something is, from its most remarkable property, that of rendering a body combustible, properly enough denominated the food of fire, the *inflammable principle*, the *phlogiston*. . . . This inflammable principle, or phlogiston, is not one thing in animals, another in vegetables, another in minerals; it is absolutely the same in them all. . . . This identity of phlogiston may be proved from a variety of decisive experiments; I will select a few, which may at the same time confirm what has been advanced concerning the constituent parts of sulphur.

"From the analysis or decomposition of sulphur effected by burning, we have concluded that the constituent parts of sulphur are two—an *acid* which may be collected, and an *inflammable principle*, which is dispersed. If the reader has yet acquired any real taste for chemical truths, he will wish to see this analysis confirmed by synthesis; that is, in common language, he will wish to see sulphur actually made by combining its acid with an inflammable principle. It seldom happens that chemists can reproduce the original bodies, though they combine together all the principles into which they have analysed them; . . . in the instance, however before us, the reproduction of the original substance will be found complete.

"As the inflammable principle cannot be obtained in a palpable form separate from all other bodies, the only method by which we can attempt to unite it with the acid of sulphur must be by presenting to that acid some substance in which it is contained. Charcoal is such a substance; and by distilling powdered charcoal and the acid of sulphur together, we can procure a true yellow sulphur, in nowise to be distinguished from common sulphur. This sulphur is formed from the union of the acid with the phlogiston of the charcoal; and the charcoal may by this means be so entirely robbed of its phlogiston, that it will be reduced to ashes, as if it had been burned. . . .

"I will in this place, by way of further illustration of the term phlogiston, add a word or two concerning the necessity of its union with a metallic earth, in order to constitute a metal. Lead, it has been observed, when melted in a strong fire, burns away like rotten wood; all its properties as a metal are destroyed, and it is reduced to ashes. If you expose the ashes of lead to a strong fire, they will melt; but the melted substance will not be a metal, it will be a yellow or orange coloured glass. If you pound the glass, and mix it with charcoal dust, or if you mix the ashes of the lead with charcoal dust, and expose either mixture to a melting heat, you will obtain not a glass but a metal, in weight, colour, consistency, and every other property the same as lead. The ashes of lead melted without charcoal become glass; the ashes of lead melted with charcoal become a metal. The charcoal, then, must have communicated something to the ashes of lead, by which they are changed from a glass to a metal. Charcoal consists but of two things—of ashes and of phlogiston; the ashes of charcoal, though united with the ashes of lead, would only produce glass; it must therefore be the other constituent part of charcoal, or phlogiston, which is communicated to the ashes of lead, and by an union with which the ashes are restored to their metallic form. The ashes of lead can never be restored to their metallic form without their being united with some matter containing phlogiston, and they may be reduced to their metallic form by being united with any substance containing phlogiston in a proper state, whether that substance be derived from the animal, vegetable, or mineral kingdom; and thence we conclude not only that phlogiston is a necessary part of a metal, but that phlogiston has an identity belonging to it, from whatever substance in nature it be extracted. And this assertion still becomes more general if we may believe that metallic ashes have been reduced to their metallic form, both by the solar rays and the electrical fire."

(To be continued.)

THE ELECTROLYTIC DEPOSITION OF ZINC,
USING ROTATING ELECTRODES.*

By T. SLATER PRICE, D.Sc., and G. H. B. JUDGE.

Under ordinary conditions zinc cannot be quantitatively deposited from a pure solution of zinc sulphate, or from one containing a small proportion of free sulphuric acid. An examination of the literature shows that although various methods have been worked out, using rotating electrodes and solutions of zinc sulphate to which some foreign electrolyte, such as oxalic acid, sodium acetate, &c., has been added, only two investigators have endeavoured to deposit zinc from the pure solution of the sulphate. Denso (*Zeit. Elektrochem.*, 1903, ix., 463), using a very imperfect method of stirring the electrolyte, was unable to obtain good results, although he could satisfactorily deposit cadmium from slightly acid solutions of the sulphate. Kollock and Smith (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1255) obtained quantitative results, even in the presence of free sulphuric acid, using a mercury cathode and rotating anode; we shall have occasion to refer to this later.

We have investigated the deposition of zinc from solutions of zinc sulphate, making use of a rotating cathode, and the present communication gives a summary of the results so far obtained.

The platinum electrodes used were similar to those described in F. Mollwo Perkin's "Practical Methods of Electrochemistry," p. 81; the sand blasted gauze cathode was 22 m.m. in diameter, and 40 m.m. long; the double ring of wire with baffle plates, forming the anode, was 40 m.m. in diameter. For rotating the cathode use has been made of the front hub of a bicycle. This was suggested to one of us by Mr. H. L. Heathcote, B.Sc., the chief chemist at Rudge-Whitworth, Ltd., and we have found that it works extremely well, and, moreover, has the advantage of being cheap. One end of the spindle is drilled to receive the cathode, which is fastened in position by means of a screw, as shown in Fig. 1; or the spindle may be fitted with a small chuck for holding the cathode. The other end of the spindle is fitted with a grooved pulley. In order to make connection with the source of current two spokes are soldered across the hub, the one being bent and connected with the negative leading wire. The ball bearings are lubricated with a mixture of graphite and oil. The whole arrangement is practically frictionless, and can be driven by means of a small motor which works with 4 to 6 volts, and only costs 8s. 6d. The drop in potential across the bearings varies from one half to one volt.

In working with rotating cathodes we have not found it convenient to use a beaker to hold the solution. After the electrolysis is finished it is not satisfactory to stop the cathode rotating in order to syphon off the electrolyte and at the same time run in distilled water till all the solution has been displaced. It often happens that a trace of metal is re-dissolved from the cathode. If the beaker is to be so wide that the syphon tube can be put down between it and the anode, the cathode being kept rotating, the volume of the solution becomes inconveniently large. An ordinary tap funnel, as shown in the figure, answers admirably in place of the beaker. The one we have used has a capacity of about 100 c.c., and the anode ring just fits into it. The suction caused by the rotating cathode continually draws up the liquid from the neck of the funnel just above the tap, so that the circulation of the electrolyte is complete. We have tested this by putting a little chloroform into the neck, and then water above it; on rotating the cathode all the chloroform was rapidly drawn up and mixed with the water.

In all our experiments the volume of the solution was 50 to 60 c.c., and during the electrolysis the mouth of the funnel was covered by means of a split cover glass; towards the end of the experiment the cover glass and the sides of the funnel were washed down with distilled water, and the

current passed for a short time longer in order to make sure that deposition was complete. The cover glass was then removed, and the washing of the cathode commenced at the same time as the tap of the funnel was turned in order to let the solution run out. The washing was continued until the current had fallen to zero, the cathode continuously rotating meanwhile. The electrode was then washed with absolute alcohol, and dried at steam-heat. In all cases the cathode was silvered before deposition of the zinc upon it.

The first experiments were made without taking any precautions to keep the electrolyte cool. The solution of zinc sulphate does not conduct very well, and it was found that if the voltage used was high enough to give a current of 2 amperes at the commencement of the experiment, the deposit was very liable to be spongy. The method finally adopted was as follows:—At the commencement of the experiment the current used was 0.25 ampère, the voltage necessary being 4; after five minutes the current was raised to 0.5 ampère, the necessary voltage being 5 to

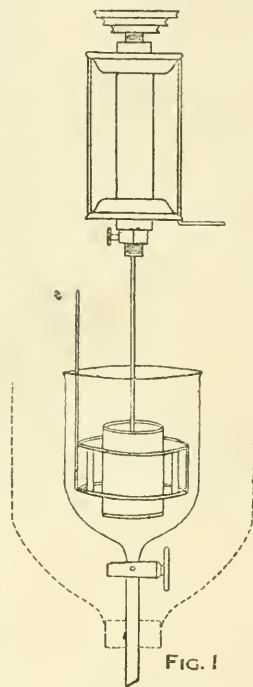


FIG. 1

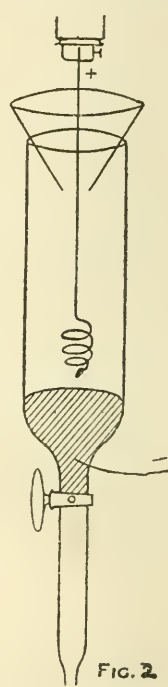


FIG. 2

5.5; after five more minutes the current was made equal to 1 ampère and the voltage was 6 to 6.5. If the apparatus was then left to itself the current gradually increased to 2 amperes (in about ten minutes), owing to the increase in conductivity, due partly to the liberation of sulphuric acid as the zinc is deposited, and partly to the heating effect of the current. The current was then kept at 2 amperes for twenty minutes (voltage finally 4.5 to 5.5), the cover glass and sides of the funnel being washed down about five minutes before the end of the experiment. The current could have been raised to 2 amperes in a shorter time than given above, but our object was not to cut down the time of deposition to a minimum, but rather to get a quantitative result.

The weight of zinc taken in each case was 0.2275 gm., and the weights of zinc deposited were 0.2257, 0.2251, 0.2258, 0.2249, gm. respectively. The deposit was very fine in appearance, of a light grey colour, and quite firm and adherent. In each case the solution was tested with ammonium sulphide, and no zinc could be detected. The results, although agreeing among themselves, were, how-

* A Paper read before the Faraday Society, June 12, 1906.

ever, uniformly low. It was afterwards found that the test with ammonium sulphide was not delicate enough, and that potassium ferrocyanide in hydrochloric acid solution must be used in its place. During the experiment the solution became quite warm, and it was possible that the low result was due to the increased solvent action of the free sulphuric acid on the deposited zinc (this statement is simpler than discussing the alteration with the temperature of the deposition potential of the zinc and hydrogen ions respectively). This was tested by increasing the current during the latter part of the experiment, the solution thereby being heated to a still higher temperature. With 4 ampères the weights of zinc deposited were 0.2230 and 0.2220 grm. respectively; with 5 ampères 0.2209 grm. The low result was evidently due to the heating effect of the current.

In the next experiments the electrolyte was kept cool by means of a jacket containing ice, as shown by the dotted lines in Fig. 1. The tap of the funnel could easily be turned by means of a glass rod, which hooked into a loop put on to one end of the tap.

The results obtained were very satisfactory. The weight of zinc taken in each case was 0.2274 grm. The weights found were 0.2274, 0.2266, 0.2271, 0.2260, 0.2274, 0.2268, 0.2273, 0.2272, 0.2269 grm. respectively. The temperature of the solution did not rise above 14° C.; the number of revolutions per minute of the cathode varied from 300 to 500, and in each case the deposit was very good. At the end of the experiment the normality of the solution with respect to sulphuric acid would be somewhere about N/20; it cannot be accurately given owing to the dilution on washing down.

It was even found possible to add a certain amount of sulphuric acid to the solution of zinc sulphate used, as shown by Table I. The normality of the solution with respect to sulphuric acid is that before the electrolysis was started. After washing down it would be diminished by about one-third, neglecting the acidity due to the sulphuric acid formed from the zinc sulphate. The first four experiments gave good results; in the last two the concentration of the acid was too great.

Instead of cooling with ice, cooling by means of a continuous flow of water through the outer vessel was tried, with the following results:—Weight of zinc taken was 0.2274 grm. The weights found were 0.2270, 0.2271, 0.2265, and 0.2261 grm. respectively. In the last two cases a specially made jacketed funnel was used, but it did not show any advantage over the arrangement shown in the diagram. The temperature in any of the four experiments did not rise above 17° C.

Table II. gives a series of results obtained when various salts were added to the solution of zinc sulphate. In each case the experiment was started with a low current, which was then gradually increased to 2 ampères; t_1 is the time in minutes taken to increase the current from 0.5 to 2 ampères, and t_2 the time the current was kept at 2 ampères. The solution was not cooled, and the weight of zinc taken in each case was 0.2274 grm.

The deposits were all that could be desired in every case where sodium sulphate was present, but where sodium acetate alone was added the deposit was liable to be spongy, and even if it was adherent, it was of a bad colour. The table shows that good results are obtained in the presence of 2 to 3 grms. of sodium sulphate, with or without sodium acetate, but that it is not advisable to have any free sulphuric acid present to start with. Exner (*Journ. Am. Chem. Soc.*, 1904, xxv., 896), Ingham (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1269), and Fisher and Boddaert (*Zeit. Electrochem.*, 1904, x., 945), use sodium acetate (1 to 3 grms.) and acetic acid (0.2 c.c. of 30 per cent acid), and rotating anode; in the present case it is preferable to replace some or all of the sodium acetate by sodium sulphate, and the addition of acetic acid is unnecessary. Even with currents of 3 ampères, when the temperature rises to 45° C., good results are obtained in the presence of 2 grms. of sodium sulphate plus 1 grm. of sodium acetate.

TABLE I.

Weight of zinc taken.	Normality of acid.	Weight of zinc found.	Error.
Grm.		Grm.	Grm.
0.2275	N/15	0.2261	-0.0014
0.2275	N/15	0.2275	0.0000
0.2275	N/7.5	0.2267	-0.0008
0.2275	N/6	0.2271	-0.0004
0.2275	N/4	0.2255	-0.0020
0.2275	N/3	0.2193	-0.0082

TABLE II.

Grms. of Na_2SO_4 .	Grms. of sal. acetate.	C.c. of 2N H_2SO_4 .	t_1 .	t_2 .	Volts.	Weight of Zn found.	Error.	Temperature of the solution rose to—
1	—	—	10	19	3.5—6.8	0.2269	-0.0005	
2	—	—	6	17	3—5.8	0.2274	0.0000	27°
3	—	—	4	16	3.5—5.3	0.2277	+0.0003	
—	1	—	11	19	4.5—8	0.2266	-0.0008	
—	2	—	5	16	4—6.8	0.2276	+0.0002	
2	1	—	7	13	3.5—5.8	0.2276	+0.0002	28°
3	—	5	5	17	3.5—4	0.2262	-0.0012	
3	—	5	6	20	3.5—4.3	0.2259	-0.0015	
3	—	5	6	11	3.8—4.5	0.2213	-0.0061	
3	—	10	—	25	3.5—4	0.2187	-0.0087	
—	3	5	5	19	4—6	0.2278	+0.0004	
2	1	2	4	18	4.3—5.5	0.2262	-0.0012	31°
2	1	5	5	16	4.5—5	0.2235	-0.0039	
2	1	5	4	20	4.3—5	0.2206	-0.0068	
1	2	5	8	17	5—6	0.2250	-0.0024	
2	2	5	6	18	3.8—5.5	0.2245	-0.0029	
(a) 2	—	—	—	—	—	0.2252	-0.0022	42°
(a) 2	1	—	—	—	—	0.2278	+0.0004	45°

(a) In these two cases the current was allowed to rise to 3 ampères.

TABLE III.

Zinc present.	Concentrated H_2SO_4 added.	Time, in mins.	Zinc found.	Error.
Grm.	40 drops = 3 c.c.			
0.2234	7	20	0.2208	-0.0026
0.2234	7	10	0.2173	-0.0061
0.2234	7	5	0.2200	-0.0034
0.2234	6	10	0.2202	-0.0032
0.2234	6	8	0.2202	-0.0032
0.2316	4	8	0.2279	-0.0037
0.2316	3	8	0.2288	-0.0028
0.2316	2	8	0.2317	+0.0001
0.2316	2	8	0.2318	+0.0002
0.2316	2	8	0.2304	-0.0012
0.2316	2	5	0.2246	-0.0070
0.3353	2	10	0.3351	-0.0002
0.3353	2	10	0.3347	-0.0006
0.2316	—	5	0.2288	-0.0028

Further experiments on the deposition of zinc, using the above apparatus, are being carried out in this laboratory, the results of which we hope to communicate later to the Society.

Kollock and Smith's method (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1255) for the determination of zinc, using a mercury cathode and a rotating anode, is a very good one, but we think that the modification of the apparatus shown in Fig. 2 makes it more convenient. According to the original paper the mercury and the zinc amalgam are both dried and weighed in the glass tube which is used for the deposition. In our experiments the mercury was weighed in a porcelain crucible, put into the electrolysis tube, and at the end of the experiment the amalgam was run off into

the crucible through the tap; it is even possible to obtain the amalgam dry in this manner, although it is not advisable to neglect washing it with alcohol and ether. It is not absolutely necessary to syphon off the electrolyte and replace it by distilled water before running off the amalgam, although this latter procedure would tend to greater accuracy, obviating any carelessness in tapping off the amalgam. The figures given in Table III. were obtained in this way, *i.e.*, without syphoning off the electrolyte. They show, moreover, that it is necessary not to exceed a certain amount of free sulphuric acid, although Kollock and Smith do not mention this in their paper in the case of zinc. In each case the volume of the solution used was 10 c.c., and the current employed 5 ampères, requiring a voltage of 7.

Thus accurate results were obtained when not more than 2 drops (40 drops = 3 c.c.) of concentrated sulphuric acid were used in the presence of 0.2316 to 0.3353 grm. of zinc, the time of deposition being eight to ten minutes.

ELECTRO-CHEMICAL CALCULATIONS.*

By JOSEPH W. RICHARDS.

(Continued from p. 7).

VOLTAGE DROP AT THE ELECTRODE SURFACES.

THIS is the loss of potential across the electrodes corresponding to the work done at the electrodes. It is practically determinable by measuring the total potential drop, and subtracting from it the drop due to overcoming the ohmic resistance of the electrolyte. Calling V the total drop of potential, and V^d that part of it absorbed in chemical (or physical) work at the surface of the electrodes, then—

$$V^d = V - V^c.$$

If V^c has been determined in the manner described in the last paragraph, or has been calculated from the specific resistance of the electrolyte, properly determined, and the resistance capacity of the electrolytic vessel, then V^d represents accurately the voltage drop due to all phenomena occurring at the surface of the electrodes, as distinguished from the mere phenomenon of electric conduction, ruled absolutely by Ohm's law, occurring in the body of the electrolyte.

It may not be amiss to remark, *en passant*, that the fact that Ohm's law applies absolutely to the conduction of electricity through the body of an electrolyte, in the same manner as in a metallic conductor, combined with Prof. Hopkins's recent determinations that the conducting of the current is practically instantaneous in electrolytes, as it is in solids, and that the body of an electrolytic conductor acts in all respects magnetically, &c., exactly the same as the body of a metallic conductor—all prove the identity of the mechanism of electric conduction through the substance or body of an electrolytic conductor and through solid metallic conductors. The phenomena at the bounding surfaces, the electrodes, are different in the two cases, but there is no experimental evidence of any dissimilarity in the mechanism of the conduction in the body of the conductors in the two cases.

TRANSFER RESISTANCE.

This is supposed to represent resistance to the passage of the current from the electrolyte to the electrode, of the nature of the work done when current is passed across a thermo-electric junction; that is, it is a resistance purely physical in its nature, existing simply because the current passes from one conducting substance to another one, and, finally, a resistance which causes the current to either generate heat, by heating this junction, or to absorb heat, by cooling the junction. It is therefore a reversible phe-

nomenon, either subtracting potential from the current in such quantity as that the heat thus generated represents the heat equivalent of the watts thus lost, or else contributing potential to the circuit in such quantity that the potential thus furnished represents, when multiplied by the ampères flowing, the watt equivalent of the heat energy absorbed.

In your lecturer's opinion, this transfer resistance must be very small. Since it would be of different signs at the two electrodes, absorbing voltage at one and generating nearly an equal amount at the other, the difference between two quantities in themselves small, must be of a low order of magnitude. Further, no reliable determinations are at hand concerning these + and - thermo-electrical potentials, because of the inevitable complication of the measurements by purely chemical changes. For instance, one investigator kept two zinc electrodes in zinc-chloride solution, but at 20° C. difference of temperature, and measured the difference of voltage, calling it thermo-electric difference of potential; but aside from the fact that this ignores any thermo-electric difference of potential between the hot and the cold solutions or in any part of the external circuit, it is certain that it ignores the difference between the heat of formation of zinc chloride in aqueous solution at two temperatures 20° apart, which might easily be equal to the whole potential difference noted. Until, therefore, physicists have cleared up satisfactorily this whole subject of thermo-electric potential between electrodes and solutions, we are making a less error in leaving out its consideration than in trying to account and allow for it—particularly since we know that some of the so-called allowances are certainly erroneous.

I have left out of the definition of transfer resistance that produced by a change in the electrode whereby a film of insoluble salt or gas is produced and so chokes off the current. Such action is polarisation, and such change in the original conditions, practically introducing modified or even new electrode surfaces, is not transfer resistance, properly speaking.

VOLTAGE REQUIRED FOR CHEMICAL WORK.

WE arrive here at the kernel of electrolytic calculation, the sole and sufficient basis being that the amount of electrical energy expended in doing chemical work must equal the energy equivalent of the chemical work done. If that position does not hold in this question, then energy could be created or lost, and the principle of the conservation of energy violated. We must admit, however, that if an electrolytic cell cools off while the current is passing, that external heat energy is being supplied which will diminish, by the amount so supplied, the work being done by the current. However, that quantity is in the nature of a possible correction, while the heat of the chemical reaction produced is the principal factor.

We must remark at the outset that the chemical work done means the whole change from the system before electrolysis to the system after electrolysis. There is no division of the chemical work of the current into that required for assumed primary reactions and that for assumed secondary reactions. Only changes taking place at the surface of the electrodes, however, affect the energy requirements; chemical reactions taking place away from immediate contact with the surface of the electrodes neither absorb energy from the circuit nor deliver energy to it,—they are purely incidental and independent chemical phenomena.

Knowing that 96,540 coulombs set free one chemical equivalent weight in grms. of an element, or decompose one chemically equivalent weight in grms. of a substance, or, in more general terms, reduce by one valency atomic weight of any chemically basic element, or increase by one valency atomic or molecular weight of any chemically acid element or radical,—we can soon foot up the chemical energy of the change produced. The thermochemical heat absorbed in the separation of a chemical equivalent weight of an element is the energy required to isolate it; and since the passage of 96,540 coulombs produce that

change, the voltage drop must be such that the calculated heat equivalent of the electric energy expended—

$$96,540 \times \text{voltage drop} \times 0.2385$$

is equal to the thermochemical heat absorbed (Q for 1 equivalent). The voltage drop for the decomposition (V_d) must therefore be—

$$\text{Voltage drop} = \frac{Q \text{ for 1 equivalent}}{23,040}$$

These calculations have been made and verified by experiment on many chemical compounds. There are some few exceptions, but many such have subsequently been shown to be only apparent exceptions, the real reaction occurring during electrolysis not having been exactly understood, or else the thermochemical data not applying strictly to the conditions under which electrolysis took place.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 21st, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

(Concluded from p. 9).

131. "Improved Apparatus for the Determination of Molecular Weights." By PHILIP BLACKMAN.

Isotonic solutions of two substances in the same solvent have equal vapour pressures at the same temperature. The state of equilibrium is represented by the equation:—

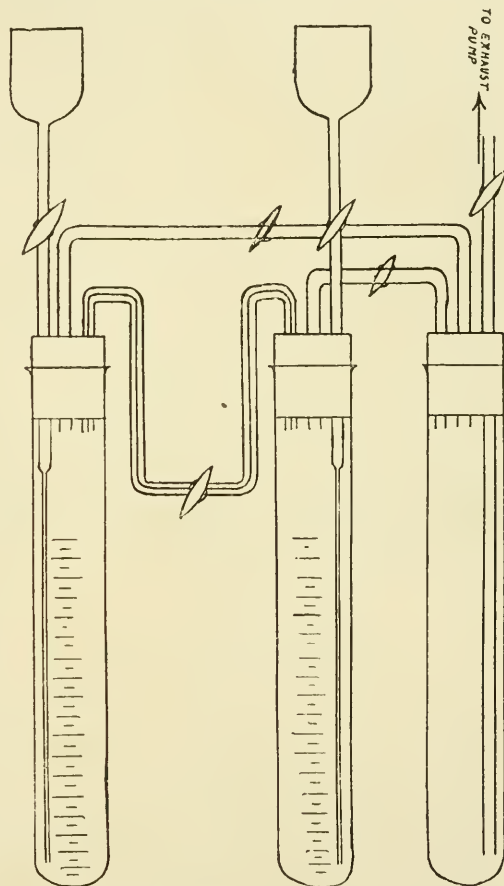
$$\frac{m_1}{m_2} = \frac{w_1}{w_2} \cdot \frac{v_2}{v_1}$$

(w_1, w_2 are the weights of the substances of molecular weights m_1, m_2 , dissolved in the solvent of volumes v_1, v_2 respectively). If two such solutions, maintained at the same temperature, have their vapours in communication by means of a suitable gauge, the indicator will remain stationary.

Unlike the previous method described by the author (*Trans.*, 1905, lxxxvii., 1474; *Proc.*, 1905, xxi., 304), the success of which depends entirely on the regularity with which the solutions can be made to boil, the new method is free from this difficulty.

Two graduated boiling tubes, and another similar ungraduated tube, are each fitted with a three-holed rubber stopper; through each stopper of the graduated tubes passes a glass-stoppered dropping funnel, the lower end of which is drawn out to a fine point which reaches to the bottom of the tube (a piece of glass tubing, drawn out to a point, may also be fixed by a rubber connection to the

end of the funnel just below the stopper). The two graduated boiling tubes are connected by a gauge fitted with a tap, a suitable liquid which is not affected by the vapour of the solvent being used as indicator. These two tubes are connected with the third tube by means of inverted U-pieces, also fitted with taps. The third tube is furnished with a glass-stoppered tube. The three tubes should be arranged in the form of a triangle, so that the apparatus is self-supporting (see figure).



By using equal weights of the substances whose molecular weights are to be compared, the calculations are considerably simplified; the above equation, by making $w_1 = w_2$, becomes $m_1/m_2 = v_2/v_1$.

Substances. (Those marked with asterisks * were set as tests).

		Ratio m_1/m_2 .	
		Theoretical.	Found.
<i>p</i> -Dibromobenzene ($= m_1$)		1.50	1.48
Bromo- <i>a</i> -naphthol ($= m_1$)		1.42*	1.41
Bromo- <i>a</i> -naphthol ($= m_1$)		1.10*	1.13
Picric acid ($= m_1$)		1.13	1.12
2 : 4-Dinitrotoluene ($= m_2$)		1.30*	1.32
2 : 4-Dinitrotoluene ($= m_1$)		1.27*	1.25
<i>p</i> -Chloroaniline ($= m_2$)		1.59*	1.55
<i>p</i> -Chloroaniline ($= m_2$)		1.08*	1.09
Iodoform ($= m_1$)		2.14	2.09
Hydrazobenzene ($= m_2$)		1.34	1.35
1-Bromo-2 : 4-dinitrobenzene		1.46	1.50
β -Naphthylamine ($= m_2$)		1.60	1.59
<i>p</i> -Chloroaniline ($= m_2$)		1.12*	1.19
<i>p</i> -Toluidine ($= m_2$)		1.33	1.34
<i>m</i> -Dinitrobenzene ($= m_1$)		1.22	1.21
<i>p</i> -Chloronitrobenzene ($= m_2$)			
<i>p</i> -Chloronitrobenzene ($= m_2$)			
1-Chloro-2 : 4-dinitrobenzene			
1-Chloro-2 : 4-dinitrobenzene			
<i>p</i> -Dibromobenzene ($= m_1$)			
<i>a</i> -Naphthylamine ($= m_2$)			
1-Chloro-2 : 4-dinitrobenzene			
<i>p</i> -Nitroaniline ($= m_1$)			
Hydrazobenzene ($= m_2$)			
1-Bromo-2 : 4-dinitrobenzene			
Diphenylamine ($= m_2$)			
Picric acid ($= m_1$)			
β -Naphthylamine			
<i>a</i> -Naphthylamine ($= m_1$)			
<i>p</i> -Nitrotoluene ($= m_2$)			

The weighed quantities of the two substances (about 0.1–0.5 gm.) are introduced into the graduated boiling tubes, the stoppers fixed in position, and the necessary connections effected. The taps in the funnels and gauge are kept closed, those in the U-tubes and remaining tube being left open; a little of the solvent is added to the funnels to ensure that no air may find its way into the apparatus. The third tube is then connected, by means of the stoppered tube, with a pump, and as high a vacuum as possible is obtained, after which the taps in the inverted U-pieces are closed. The solvent is now added from the funnels, care being taken to avoid the introduction of air. The solvent must be added in sufficient quantity to cover the lower ends of the funnels. The substances must be left to dissolve, the process being hastened by slightly agitating the apparatus; this also assists in producing uniformity of concentration. The tap in the gauge is cautiously opened (if care is not taken, the liquid serving as index may be forced into one of the solutions), and the movement of the indicator observed. This moves towards the tube in which the vapour pressure is smaller; consequently, if the solvent is added drop by drop from the funnel to that tube, a stage is reached at which the indicator remains stationary. Equilibrium having been attained, the volumes of the solutions are read off. More liquid may now be added to one of the solutions, and equilibrium re-established by the addition of solvent to the other, when another reading of the volumes is taken. This process is repeated as often as is desirable.

It may be advantageous to maintain the solutions at equal temperatures by standing the apparatus in a trough of water.

The accompanying table shows the results which were obtained. Equal weights of the substances were used in each experiment, the solvent was ether, and concentrated sulphuric acid was used as the index.

(We are indebted to the author for permission to insert the woodcut illustrating this paper).

PHYSICAL SOCIETY.

Ordinary Meeting, June 22nd, 1906.

Prof. J. PERRY, F.R.S., President, in the Chair.

A PAPER ON "*The Effect of Radium in Facilitating the Visible Electric Discharge in vacuo*" was read by Mr. A. A. CAMPBELL SWINTON.

It has been shown by Edison, Fleming, and others, that the passage of the electric discharge *in vacuo* is much facilitated by heating the cathode. More recently, it has been shown that the passage of the discharge is still further facilitated by coating the heated cathode with oxides of the alkaline metals. It is generally held that the efficacy of the hot oxides in this direction is due to their giving off negatively-charged ions or corpuscles. The author therefore decided to ascertain whether similar effects could be obtained by painting the cathode with radium, and as radium gives off corpuscles when cold, it was anticipated that it might not be necessary to heat the cathode. Using a continuous current up to 400 volts pressure, this was found not to be the case, the radium having no appreciable effect in producing a visible discharge. When the radium-coated cathode was heated to redness, the radium was found to have a very marked action in facilitating the production of a luminous discharge. Experiments were made which proved that the mere presence of radium in the tube was insufficient to produce the effect, and, furthermore, it was found that the tube would only allow visible discharges to pass in the direction that made the radium-treated electrode the cathode, the tube acting as a unidirectional valve in the same way as do tubes with cathodes coated with oxides. Experiments were also made without any heating of the cathode, but using alternating currents of higher voltages than were available in continuous current. It was found that using an untreated electrode it required

from 800 to 900 volts to get a visible discharge to pass; whereas, using a radium-treated electrode, a visible discharge could be got to pass with from 700 to 800 volts. The exact voltages required in each case were variable, but it was always found that a visible discharge could be got to pass, using the radium-treated electrode, with about 100 volts less than when the untreated electrode was employed. The phenomena with continuous currents, as described in the paper, were illustrated experimentally.

A paper on "*The Effect of the Electric Spark on the Activity of Metals*" was read by Mr. T. A. VAUGHTON.

It has been pointed out by several observers that some metals, such as aluminium, cadmium, zinc, magnesium, &c., although not radio-active in the ordinary sense of the word, yet have the power of affecting a photographic plate. The electric spark has a remarkable influence on this "activity," in some cases causing an increase, and in others apparently diminishing it. The alteration is not merely momentary but remains for months. It is, however, quite superficial, and may be removed by slightly rubbing the surface of the metal with emery-paper. In the case of aluminium sparked with gold, the direction of the current does not make much difference in the activity of the sparked plate, but in the case of other couples the difference is very marked. For example, if a cadmium strip is sparked with antimony, the cadmium being connected with the positive terminal, the cadmium becomes very active photographically, not only on the spot sparked but all over its surface. If, however, the cadmium is connected with the negative terminal and sparked with a positive terminal of antimony, the cadmium remains very slightly more active than if not sparked at all. In order to compare the effect of the spark on the "activity" of various metals, plates of the following fifteen elements were prepared:—Magnesium, aluminium, iron, cobalt, nickel, copper, zinc, silver, cadmium, tin, antimony, platinum, gold, lead, and bismuth. Each plate was sparked with a terminal of each of the fifteen metals in the order of their atomic weights. After sparking, the plate was placed on a sensitive bromide plate, and left in the darkness for a month. It was found that in the case of Al, Ni, Mg, and Sn the sparked spots were more active than the rest of the plate; but with Zn, Cd, Pb, and Bi the spots are not so active as the rest of the plate—probably resulting from an opaque film of oxide produced at the sparking-point. The penetrating power of the rays emitted from sparked metals varies considerably, and is investigated in the paper. The author points out that it is interesting to note that most of the greatest increases in activity, caused by sparking, are produced in sparking together two metals the sum of whose atomic weights approaches that of a radio-active element, thus suggesting a synthesis of these elements.

A paper on "*The Dielectric Strength of Thin Liquid Films*" was read by Dr. P. E. SHAW.

The range of voltage used in the experiments is from 25 to 400, and the corresponding spark-lengths vary from about 0.15μ to 6.0μ ($\mu = 0.001$ m.m.) for the insulating liquids used. The apparatus employed for measuring length is the micrometer designed by the author for measuring gauges (*Proc. Roy. Soc.*, April, 1906). On each micrometer-screw a cap is fitted—one cap terminates in a disc of iridio-platinum, and the other in a sphere or portion of a sphere of iridio-platinum. Discharge occurs between the two iridio-platinum surfaces, a drop of the insulating liquid being placed between them. Voltage is registered by a voltmeter, and is obtained by passing an electric-lighting current through a liquid resistance, and taking whatever fraction of the voltage is required. Two circuits are used, one of very low voltage, say, $\frac{1}{10}$ volt, to determine the contact position for the surfaces, and the other to give the high voltage required for sparking. The substances used were olive oil, castor oil, linseed oil, rape oil, turpentine, fusel oil, oil of resin, cod-liver oil, neat's-foot oil, paraffin, transformer oil, the homologous series C_5H_{12} , C_6H_{14} , C_7H_{16} , C_8H_{18} , and armacell, ohmaline, and Sterling

varnishes. The best insulators are paraffin and transformer oil, though for these, as for all commercial oils, great care was taken to remove water and acid by prolonged heating to 110° C., and treating with potassium carbonate. Generally speaking, the curves connecting voltage and spark-length are roughly straight to the origin, the gradient varying between 110 volts per micron and 70 volts per micron. Distinct local variations in gradient are found in one or two cases, e.g., castor oil, olive oil, and paraffin. The air-curve is cut by the oil-curves at voltage 300; for less voltage air has greater dielectric strength, but at that voltage air suddenly weakens, and for greater voltages all oils are stronger. No simple connection can be traced between specific inductive capacity and dielectric strength.

Mr. A. RUSSELL considered the method of research a valuable one. He doubted, however, whether the results obtained would be much help in determining the relative values of the "dielectric strengths" of thin films of insulating materials. The numbers given in the paper only refer to thin films between iridio-platinum electrodes. Hobbs has shown that for small distances the sparking potentials are practically independent of the nature of the gas between the electrodes. They depend mainly upon the metal of which the electrodes are made. At these microscopic distances, owing to the corpuscles, the electrostatic field between them was far from uniform. The disruptive voltage for a film of air one micron thick, if it could be subjected to a uniform electrostatic stress, would only be about 3.8 volts. When liquids were introduced between the electrodes, it was extremely difficult to determine the maximum electric intensity at the instant of discharge, as they had a different dielectric coefficient from air, and so there would be refraction of the Faraday tubes.

Dr. SHAW, in reply to Mr. Russell, said that the air-curve mentioned was that for iridio-platinum, and was obtained by a distinct set of experiments on air. The gradient was steeper than any found by Hobbs in his recent work. As regards the use of the term "dielectric strength," Dr. Shaw used it in its common sense as a general term implying strength to resist discharge, and no numerical value was given to it in the paper.

A paper on "*The Effect of Electrical Oscillations on Iron in a Magnetic Field*" was read by Dr. W. H. ECCLES.

In attempting to make precise measurements of the effect of high-frequency oscillations on iron held magnetised by a magnetic field, two main difficulties are met. The one is that arising from the fact that the oscillatory currents induced on the surface of the iron investigated shield the inner layers, and thus make the mass of iron affected a variable quantity. The other difficulty arises in the matter of producing oscillations of determinate and invariable character. The author has endeavoured to meet the first difficulty by using oscillations so feeble that they affected only the outermost layers of the iron wires employed, and these even only slightly. The second difficulty has been met by using the oscillations produced in an open insulated solenoid by a single small measurable spark passed to one end of the solenoid.

In the experiments, soft iron was taken a large number of times round any chosen magnetic cycle till what may be called a cyclic state was attained. The field was then given any desired value, and the iron submitted to a train of oscillations. The consequent alteration in pole strength was observed by the deflection of a magnetometer-mirror. These processes were all repeated a number of times for each selected point of the cyclic curve. The apparatus used consisted of two straight solenoids placed horizontally on one and the same magnetic east-west line on either side of the magnetometer. They were connected in series with cells, rheostats, measuring-instruments, &c. The coil in which the oscillations were generated was inside the east solenoid, but well insulated from it; one end was free, and the other was connected to one side of a micro-meter spark-gap. The sparks were produced by a diminutive

influence-machine, and were usually half a millimetre in length. After arranging the two empty solenoids in compensating position, equal amounts of iron wire were introduced into them, and adjusted till only trifling magnetometer deflections accompanied the rise and fall of the solenoid current. The magnetometer control field could then be greatly diminished. Of course the iron in the east solenoid lay within the oscillation-coil described above. Thus, when a spark passed, the small change in the magnetic state of the east iron could be measured.

The tables of results and the diagrams from them show that the change of pole-strength produced by a spark was, at any point of a cycle, always such as to move the representative point on the IH diagram towards the centre-line of the hysteresis loop. They show, moreover, that in cycles of greater amplitude the oscillations have, on the whole, greater effects. In all cases the effects show some relation to the gradient, at the corresponding point, of the cyclic curve. In the paper the gradient curves are compared with the spark-effect curves, with the result that the spark-effect does not seem to be simply proportional to the gradient. In addition, observations on the result of varying the spark-gap are recorded. These point to the conclusion that the wastage, instigated by the oscillations, of the intrinsic energy of the magnetised material is, for certain initial voltages of the oscillations, proportional to the total energy of the oscillations.

Mr. A. CAMPBELL expressed his interest in the paper, and asked for the magnitude of the change of pole-strength produced by the passage of a spark.

Mr. WALTER congratulated the author upon the method of the research, and said that the precautions which had been taken rendered the results free from suspicion.

Dr. ECCLES, in reply to Mr. Campbell, said that the deflections produced by the change in pole-strength consequent on the passage of a spark were about $\frac{1}{8}$ of the maximum deflections obtained in the hysteresis curves.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

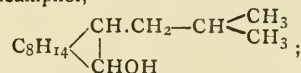
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii, No. 24, June 12, 1906.

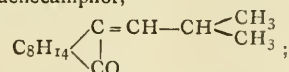
Products of the Reaction of Sodium Isobutylate and Propylate on Camphor at a High Temperature.

—A. Haller and J. Minguin.—The authors investigate the various derivatives which are formed during the reaction of camphor on certain sodium alcoholates at a high temperature. He thus prepares—

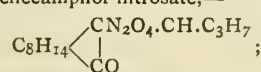
(1) Isobutylcamphol,—



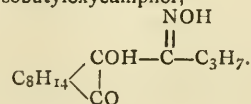
(2) Isobutylidenecamphor,—



(3) Isobutylidenecamphor nitrosate,—



(4) Isonitroso-isobutylloxycamphor,—



Magnetic Properties of Boron and Manganese Compounds.—Binet du Jassonneix.—The reduction of manganese oxides by boron in the electric furnace results in a mass containing a maximum of 28.6 per cent of boron and from which two definite borides, MnB and MnB_2 , can be separated. These borides oxidise in air, and melt at a temperature too high to allow of examination *in vacuo*. Also the difficulty of obtaining them in ingots of convenient dimensions renders it only possible to study them in the form of powder. The author finds, however, that MnB is the only compound possessing magnetic properties, and the magnetic permeability of the borated melts of manganese is greater as it contains more of this boride.

Iodomercurates of Magnesium and Manganese.—A. Duboin.—In the same way as the author prepared the iodomercurates of the alkaline earths he now prepares iodomercurates of magnesium and manganese by dissolving alternately in a small quantity of water iodine and mercuric iodide, helping the solution towards the close of the operation by a slight elevation of temperature, and then adding the iodide of magnesium or manganese. The iodomercurate of magnesium is crystalline in large crystals having a density of 3.8 and a formula $MgI_2 \cdot 2HgI_2 \cdot 7H_2O$. A second crop of very deliquescent crystals of formula $MgI_2 \cdot HgI_2 \cdot 9H_2O$ can also be obtained. The manganese salt has formula $HgI_2 \cdot 1.40MnI_2 \cdot 10.22H_2O$ and a density of 2.98, and after evaporation in dry air in presence of sulphuric acid a salt of density 3.8 and formula $3MnI_2 \cdot 5HgI_2 \cdot 20H_2O$ is obtained. In presence of water and other solvents these iodomercurates behave very much in the same manner as the calcium iodomercurates.

Reduction of Antimony Selenide.—P. Chrétien.—Antimony selenide may be completely reduced by hydrogen in the same manner as the sulphide, but the reaction is much slower. The author's investigations on this reaction and the fusibility curve of mixtures of antimony and selenium point to the existence of a number of sub-selenides, from which the author isolates the monoselenide, $SbSe$; the subselenide, Sb_4Se_3 or $Sb_2Se_3 \cdot 2SbSe$; and the saline selenide, Sb_3Se_4 or $Sb_2Se_3 \cdot SbSe$.

Bleaching of Linen.—Léo Vignon and J. Mollard.—The authors investigate the action of gaseous chlorine, chlorine water, and chloride of lime on linen. The experiments are made under definite and different conditions, allowing for the chemical and physical modifications by each process afforded by the initial properties of linen. They find that chlorine when acting upon linen modifies it and is dissolved. The linen takes new properties on itself. In particular it loses 10 per cent of its weight, takes dyes easily, giving darker and more brilliant shades.

Estimation of Albuminoid and Gelatinous Matter by means of Acetone.—F. Bordas and M. Touplain.—The authors find that by using aqueous acetone, albuminoid and gelatinous substances are precipitated from solution. Acetone also separates from fats and oils of resin the soluble salts which they may contain, and this reaction takes place without lengthy previous desiccations.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Kelp.—Can any reader give particulars as to the amount of "kelp" annually produced in England, and its commercial value?—B. M.

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THE CHEMICAL NEWS.

VOL. XCIV., NO. 2434.

NOTES OF A COURSE OF LECTURES ON THE OLD AND NEW CHEMISTRY.*

I. EXTRACTS FROM DIFFERENT AUTHORS RELATING TO THE OLD CHEMISTRY.

By Prof. Sir JAMES DEWAR, F.R.S., &c.

(Continued from p. 17).

The Revived Theory of Phlogiston.—Odling.

"THE foregoing account by Dr. Watson is almost a translation from Stahl's *Zymotechnica Fundamentalis, simulque experimentum novum sulphur verum arte producendi*, in which he establishes what may be called the permanency of chemical substance—that metallic lead is reproducible from the ashes of lead, *sulphur verum* from the acid of sulphur. And, whether or not taking note of the oxidations and deoxidations effected, how little differently, even at the present day, would the actions referred to be described and explained. Is it not our habit to say that charcoal and sulphur and lead are bodies possessing potential chemical energy, that is phlogiston; that in the act of burning, their energy which was potential becomes kinetic or dynamical, and is dissipated in the form of light and heat: that the products of their burning (including the gaseous product now known to be furnished by the burning of charcoal) are substances devoid of chemical energy, that is, of phlogiston: that when the acid substance furnished by burning sulphur is heated with charcoal, some energy of the unburnt charcoal is transferred to the burnt sulphur, just as some energy of a raised weight may be transferred to a fallen one, whereby the burnt sulphur is unburnt, provided with energy, and enabled to burn again, and the fallen weight is lifted up, provided with energy, and enabled to fall again; that the potential chemical energy of metallic lead did not originate in the lead, but is energy or phlogiston transferred thereto from the charcoal by which it was smelted; and lastly, that the chemical energy of the charcoal itself, its capability of burning, its power of doing work, in one word its phlogiston, is merely a portion of energy appropriated directly from the solar rays?

"If this be a correct interpretation of the phlogistic doctrine, it is evident that the Stahlans, though ignorant of much that has since become known, were nevertheless cognisant of much that became afterwards forgotten. For most of what has since become known, mankind are indebted to the surpassing genius of Lavoisier; but the truth which he established, alike with that which he subverted, is now recognisable as a partial truth only; and the merit of his generalisation is now perceived to consist in its addition to—its demerit to consist in its supersession of—the not less grand generalisation established by his scarcely remembered predecessors. This being so, the relationship to one another of the Stahlian and Lavoisierian theories of combustion furnishes an apt illustration of the general truth set forth by a great modern writer, that 'in the human mind, one-sidedness has always been the rule, and many-sidedness the exception. Hence, even in revolutions of opinion one part of the truth usually sets while another rises. Even progress, which ought to superadd, for the most part only substitutes one partial and incomplete truth for another; improvement consisting chiefly in this, that the new fragment of truth is more wanted, more adapted to the needs of the time, than that which it displaces.'"

* Delivered at the Royal Institution, May 19th, 1906.

CHAUCER, 1340—1400.

For out of the olde fieldes, as men saithe
Cometh all this new corn from yere to yere :
And out of olde Bookes in Goode faithe,
Cometh all this new science that men lere.

Sir priest, he said, I keep, for to have no lose
Of my craft, for I would it were kept close ;
And as you love me, kepith it secrete,
For and men knowin all my subtilte,
By God men wouldin have so grete envie
To me, because of my Philosophie,
I should be dedde, there were none otherwaie.

I woll you tell as was me taught also
The four spirites and the bodies seven
By order as I herd my lord nemene.

The first spirite quicke silvir clepid is,
The second Orpiment, the third iwis,
Sal Amoniake, and the fourth Brimstone.
The bodies seven, lo ! here 'hem anone,
Sol gold is, and Luna silver we threpe,
Mars yron, Mercury quikesilver we clepe,
Saturnus leade, and Jupiter is tinne,
And Venus copir, by my fathir kinne.

The Chanon Yeman's Tale.

LUTHER, 1483—1546.

The upright art of Alchymie liketh me well.

SHAKESPEARE, 1564—1616.

His countenance, like richest alchymy,
Will change to virtue, and to worthiness.

Jul. Cæs. i. 3.

To solemnize this day, the glorious sun
Stays in his course and plays the alchemist,
Turning, with splendour of his precious eye,
The meagre cloddy earth to glittering gold.

K. John, iii. 1.

Hence! pack! there's gold, ye came for gold, ye slaves!
You have done work for me, there's payment:

Hence!

You are an alchymist, make gold of that :—
Out, rascal dogs!

Timon, v. 1.

Full many a glorious morning have I seen
Flatter the mountain-tops with sovereign eye,
Kissing with golden face the meadows green,
Gilding pale streams with heavenly alchemy;

Sonnet 33.

Or whether shall I say, mine eye saith true,
And that your love taught it this alchemy,
To make of monsters and things indigest
Such cherubins as your sweet self resemble,
Creating every bad a perfect best,
As fast as objects to his beams assemble?

Sonnet 114.

"THE ALCHEMIST," BEN JONSON, 1574—1637.

Alchemy is a pretty kind of game,
Somewhat like tricks o' the cards to cheat a man
With charming.

He honest wretch,
A notable superstitious good soul,
Has worn his knees bare, and his slippers bald,
With prayer and fasting for it. . . . Here he comes.—
Not a profane word afore him——'tis poison.

He will make Nature ashamed of her long sleep,
When art, who's but a step-dame, shall do more
than she

In her best to love to mankind, ever could.
If his dream last he'll turn the Age to Gold.

Sir Epicure Mammon.

MILTON, 1608—1674.

So down they sat,
And to their viands fell; nor seemingly
The Angel, nor in mist, the common gloss
Of Theologians; but with keen despatch
Of real hunger, and concoctive heat
To transubstantiate: What redounds, transpires
Through Spirits with ease; nor wonder: if by fire
Of sooty coal the empirick alchemist
Can turn, or holds it possible to turn,
Metals of drossiest ore to perfect gold.

Par. Lost, b. v. 436—444.

"PARACELSUS," ROBERT BROWNING, 1812—1889.

Would I were sure to win
Some startling secret in their stead, a tincture
Of force to flush old age with youth, or breed
Gold, or imprison moonbeams till they change
To opal shafts!—Only that, hurling it
Indignant back, I might convince myself
My aims remained supreme and pure as ever!
Even now, why not desire, for mankind's sake,
That if I fail, some fault may be the cause,
That, though I sink, another may succeed?

For night is come,
And I betake myself to study again,
Till patient searchings after hidden lore
Half wring some bright truth from its prison; my
frame

Trembles, my forehead's veins swell out, my hair
Tingles for triumph. Slow and sure the morn
Shall break on my pent room, and dwindling lamp,
And furnace dead, and scattered earths and ores;
When, with a failing heart and throbbing brow,
I must review my captured truth, sum up
Its value, trace what ends to what begins,
Its present power with its eventual bearings,
Latent affinities, the views it opens,
And its full length in perfecting my scheme.
I view it sternly circumscribed, cast down
From the high place my fond hopes yielded it,
Proved worthless—which, in getting, yet had cost
Another wrench to this fast-falling frame.
Then, quick, the cup to quaff, that chases sorrow!
I lapse back into youth, and take again
My fluttering pulse for evidence that God
Means good to me, will make my cause His own.

(To be continued).

THE SOLUBILITY OF LEAD SULPHATE IN AMMONIUM ACETATE SOLUTIONS.*

By ARTHUR A. NOYES and WILLIAM H. WHITCOMB.

I. Hypotheses as to the Cause of the Solubility-increase.

It is a well known fact, and one often made use of in chemical analysis, that lead sulphate, though difficultly soluble in water, dissolves in considerable quantity in a strong ammonium acetate solution. As to the magnitude of this solubility we have, however, been able to find only two quantitative statements, that of Long (*Am. Chem. Journ.*, 1899, xxii., 217), and that of Bischof (Corney's "Dictionary of Solubilities"), both of which relate to very concentrated solutions of ammonium acetate.

There has, moreover, been offered no verified explanation of the large increase in solubility which ammonium acetate produces. It seems, however, probable that the effect arises from one of the three following causes, or from a combination of them:—(1) Lead acetate is a slightly ionised substance, and therefore a large quantity of it is produced in the solution by metathesis; (2) intermediate

cations containing lead in combination with the acetate ion, $\text{PbC}_2\text{H}_3\text{O}_2+$, are formed; (3) complex cathions of the composition $\text{Pb}(\text{NH}_3)_x++$ are produced by combination of the lead ion with the free ammonia resulting from the hydrolysis of the salt.

These three hypotheses can be tested by migration experiments, for, in the first case, the lead, being present only as an un-ionised compound, would not move at all, while in the second or third case, it would migrate with the positive current. The first and second hypotheses can further be tested by determining the degree of ionisation of lead acetate and its change with the dilution by conductivity measurements or otherwise. Furthermore, both the first and second hypotheses evidently require that sodium acetate (or any other di-ionic acetate) have nearly the same effect on the solubility of lead sulphate as ammonium acetate, while, on the other hand, the third hypothesis would lead to the expectation that the sodium salt would have a much slighter effect. The third hypothesis may seem to be inconsistent with the fact that lead hydroxide is but little soluble in ammonium hydroxide, but it is not necessarily so, since in the latter solvent the hydroxyl-ion concentration may be large enough to keep down the concentration of the lead ion, and therefore that of the complex ion, if this were not very stable. This hypothesis would, however, evidently require that neutral ammonium acetate, owing to its greater hydrolysis, be a much better solvent for lead sulphate than neutral ammonium nitrate or chloride; that these different salts behave nearly alike if a moderate proportion of ammonium hydroxide be added to their solutions; and that the addition of acetic acid greatly reduce the solvent power of ammonium acetate. These last requirements seem, indeed, to be at variance with analytical experience.

II. Previous Measurements relating to the Subject.

There already exists some evidence that lead acetate is much less ionised than other salts of the same type, and therefore that the first hypothesis furnishes the true explanation of the increase in the solubility of lead sulphate. Thus, the freezing-point measurements of Kahlenberg (*Zeit. Phys. Chem.*, 1895, xvii., 583) indicate an ionisation of only 19 per cent in $\frac{1}{4}$ molal, and of 37 per cent in $\frac{1}{2}$ molal solution. Moreover, an isolated measurement of the conductance of the salt in $\frac{1}{40}$ molal ($\frac{1}{20}$ normal) solution at 25° by Trey (*Zeit. Phys. Chem.*, 1897, xxii., 433) gave a value corresponding to an equivalent conductivity of 32.0 in reciprocal ohms or to a degree of ionisation of 28.4 per cent; and a series by Ley (*Zeit. Phys. Chem.*, 1899, xxx., 246) beginning with $\frac{1}{30}$ normal gave at this concentration an equivalent conductivity of 37.6 reciprocal ohms corresponding to an ionisation of 33.4 per cent. Evidence against the third hypothesis is furnished also by the results of Dibbitts (*Dingler Polytech. Journ.*, ccx., 475; *Zeit. Anal. Chem.*, xiii., 137), who found that sodium acetate also increases greatly the solubility of lead sulphate; he found, namely, that 100 c.c. of a solution containing 2.05 grms. sodium acetate dissolves 0.054 grm. lead sulphate, and 100 c.c. of one containing 8.20 grms. sodium acetate dissolves 0.900 grm. lead sulphate.

The subject seemed, however, to deserve fuller investigation, and we have therefore done some further work upon it. This has consisted in qualitative migration experiments with solutions of lead sulphate in ammonium acetate, measurements of the conductivity of aqueous solutions of pure lead acetate, accurate determinations of the solubility of lead sulphate in ammonium acetate solutions, and a single rough one in a sodium acetate solution. It is the purpose of this article to present the results and discuss their significance.

III. Conductivity of Lead Acetate Solutions.

The sample of lead acetate used in our experiments was prepared by crystallising the chemically pure commercial salt four times from hot water containing acetic acid, and

* From the *Journal of the American Chemical Society*, xxvii., No. 5.

once from pure water. It was dissolved in conductivity water, and the solution was standardised by precipitation with sulphuric acid and weighing the lead sulphate. Two solutions were so prepared at different times. The first contained 1.420 equivalents (0.710 mol.) per litre. The second contained 0.5088 equivalent (0.2544 mol.) per litre.

The measurements were made at 25° by the Kohlrausch method, using a resistance vessel of the Arrhenius type, the resistance capacity or cell-constant of which was determined by measurements with 0.01 normal potassium chloride solution. The results are all expressed in reciprocal ohms. The value of the equivalent conductivity (Λ_0) at infinite dilution (112.8) used in calculating the conductivity ratio (Λ/Λ_0), which corresponds to the degree of ionisation, if the salt dissociates only into Pb^{++} and Ac^- ions, was calculated from the values for the individual ions at 18° given by Kohlrausch and Grüneisen (*Berliner Sitzungsber. d. Akad. d. Wissenschaften*, 1904, p. 1221), $\Lambda_{Pb} = 61.1$ at 18°; and by Kohlrausch and Steinwehr (*Ibid.*, 1902, p. 587), $\Lambda_{Ac} = 35.0$ at 18°; and from the temperature-coefficients computed by Kohlrausch (*Ibid.*, 1901, p. 1026; *Zeit. Phys. Chem.*, xliii., 511).

The first solution above referred to was diluted four times in succession with conductivity water by means of two graduated flasks in such a way that the concentration was each time reduced to one-fourth of its former value. The value of the cell-constant (or the factor by which the actual conductance must be multiplied to give the specific conductance) in this series of experiments was 0.1389.

A second series of measurements was carried out with greater care with the second solution, it being diluted in a somewhat different manner from the first. The stock solution was kept in a Jena flask, from which it was drawn as required, air being admitted through a soda-lime tube. Two-fold dilutions were made by weighing, the volume concentrations being calculated with the help of a specific gravity determination. The value of the cell-constant was 0.1400 in the case of the first two measurements of the series, 0.1243 in the other cases.

The results of the measurements are given in Table I.

TABLE I.—Conductivity of Lead Acetate at 25°.

Equivalents per litre.	Actual conductance.	Equivalent conductivity.	Conductivity ratio $\times 100$.
<i>First Series.</i>			
0.3550	0.03457	13.50	12.0
0.0888	0.01627	25.38	22.5
0.0222	0.007035	43.74	38.8
0.00555	0.002790	68.75	60.9
<i>Second Series.</i>			
0.5088	0.04220	11.61	—
—	0.04209	11.58	—
—	0.04762	11.63	—
—	0.04772	11.66	—
—	0.04735	11.57	—
—	0.04770	11.65	—
—	Mean	11.62	10.3
0.2544	0.03345	16.34	—
—	0.03346	16.34	—
—	0.03345	16.34	—
—	0.03368	16.45	—
—	0.03361	16.42	—
—	0.03365	16.43	—
—	Mean	16.39	14.5
0.1272	0.02272	22.19	—
—	0.02274	22.21	—
—	0.02271	22.18	—
—	Mean	22.19	19.7

The mean values of the equivalent conductivity derived from these two independent series of experiments (after being corrected with help of the formula referred to just below, to a round dilution not differing much from that at

which the measurements were made) and the above mentioned results of Trey and of Ley (expressed in reciprocal ohms instead of in mercury-units as given by those authors) are for the purpose of better comparison, summarised in Table II. The table also contains the corresponding value of the conductivity-ratio ($\Lambda/\Lambda_0 = \gamma$) multiplied by 100, and the values of the empirical function $100(\gamma C)^2/C(1-\gamma)$, where C is the equivalent concentration, which function was found to be fairly constant when applied to our own data between $\frac{1}{2}$ and $\frac{1}{12}$ -normal.

TABLE II.—Summary of Equivalent Conductivity Values.

Litres per equivalent.	Equivalent conductivity.	Conductivity ratio $\times 100$.	$100(\gamma C)^2/(1-\gamma)C$.
2	11.73	10.4	0.6019 (b)
3	13.99	12.4	0.5808 (a)
4	16.47	14.6	0.6256 (b)
8	22.45	19.9	0.6148 (b)
12	26.05	23.1	0.5800 (a)
20	32.00	28.4	0.5635 (c)
32	37.63	33.4	0.5234 (d)
48	44.89	39.8	0.5461 (a)
64	46.98	41.7	0.4662 (d)
128	57.40	50.9	0.4121 (a)
192	69.94	62.0	0.5264 (d)
256	68.23	60.5	0.3623 (d)
512	79.09	70.1	0.3209 (d)
1024	89.29	79.2	0.2947 (d)

Investigator.—(a) N. and W., First Series; (b) N. and W., Second Series; (c) Trey; (d) Ley.

It will be seen from the last column that the conductivity value of Trey corresponds well with ours, but those of Ley are considerably less, especially in the dilute solutions ($1/128$ to $1/256$ normal).

The results show clearly that lead acetate is much less ionised than is usual with univalent salts, which are commonly 70 to 75 per cent ionised in 0.1 normal solution. The results of Ley with other acetates of this type show too that even these have a much higher conductivity than lead acetate; thus, for $1/32$ -normal solutions he obtained the following equivalent conductivities in reciprocal ohms:—Barium acetate, 80.0; manganese acetate, 66.6; nickel acetate, 64.6; cobalt acetate, 65.9; zinc acetate, 62.3; and cadmium acetate, 54.5; while that of lead acetate is only 37.6.

The actual values of the conductivity-ratio given in the table are not to be regarded, however, as a true measure of the ionisation, for it is very probable in view of its slight degree of ionisation that this salt forms the intermediate ion $PbAc^+$ in large quantity.

Moreover, since the Λ_0 value for dissociation into the two ions $PbAc^+$ and Ac^- would be very different from that for dissociation into the three ions Pb^{++} and $2Ac^-$, which last was assumed in computing the ratio, it is not proved by the constancy (in the stronger solution) of the function given in the last column that the former kind of ionisation alone takes place, but only that the latter kind is not the exclusive one.

IV. Migration Experiments.

Two series of qualitative migration experiments were made. In one of these, the solutions, in order to avoid stirring, were gelatinised by the addition of agar; in the other, to eliminate the possibility of any influence of the agar upon the lead salt, difference in specific gravity was alone relied upon.

In the former series a U-tube 1.75 c.m. in diameter and 15 c.m. in height was used. The bend was filled with an agar jelly made up with a normal ammonium acetate solution, and containing zinc sulphide in suspension. Above this in each arm of the tube were placed, first, a plug of jelly 0.5 c.m. long with ammonium acetate solution alone; next, one also saturated with lead sulphate; then, another one 0.5 c.m. long with ammonium acetate alone; then, one with this salt in solution and zinc sulphide in suspen-

sion; and finally, some ammonium acetate solution without agar, in which platinum-wire electrodes were placed. The tube was immersed in a bath of ice-water. The electrodes were kept at a potential difference of 80 volts for two hours, but at no point did the zinc sulphide become blackened, showing that the lead did not migrate to an appreciable extent in either direction.

Of the experiments made with solutions without agar added, only the final and most conclusive one need be described. The apparatus used consisted essentially of two U-tubes connected by side-arms, one of the tubes being joined at the bottom of the bend to a glass tube of small bore. The tubes were completely filled with half-normal ammonium acetate solution; then both arms of one of them were tightly stoppered, and by means of suction applied to both arms of the other, a normal solution of ammonium acetate saturated with lead sulphate, and strongly coloured with rosaniline hydrochloride, was slowly drawn up through the small glass tube at the bottom until the bend was sealed. The solutions had been brought to a constant temperature of 25° previous to the filling, which took place immediately over the thermostat. A difference of potential of 110 volts was applied, and the current (of 0.2 ampère) was passed for two hours. The length of the column of solution was 73 c.m., thus giving a drop in potential of 1.5 volts per c.m. The colour boundary remained sharp, and nearly stationary, showing there was no stirring. At the end of the experiment, successive portions were carefully withdrawn by means of a pipette from both arms of the tube containing the dissolved lead sulphate, almost down to the colour boundary. To each of these portions was added potassium chromate, which furnishes a very delicate test for lead even in acetate solution. None of the portions from the cathode side gave any indication of lead, even down to the line of separation. In the portions on the anode side there was a trifling quantity of lead in the portion immediately adjoining the lead sulphate solution, but a portion 2.4 c.m. away gave no precipitate whatever with the potassium chromate. An ordinary lead ion, for example, in a 0.2 normal lead nitrate solution, moves under a potential gradient of 1 volt per c.m. about 0.00040 c.m. per second, so that under the conditions of our experiment, it would have moved about $0.00040 \times 1.5 \times 7200 = 4.3$ c.m., while, in fact, no considerable quantity of the lead migrated more than a small fraction of a c.m. On the other hand, the SO_4 ions migrated several c.m. in the same time, for a precipitate of barium sulphate was obtained in all the portions from the anode arm upon the addition of barium chloride and acidifying with hydrochloric acid, while the solution in the cathode arm gave no such indication of the presence of sulphate.

Both of these series of experiments lead to the same conclusion, namely, that substantially all the lead exists in the acetate solution in the form of un-ionised compound.

V. Experiments on the Solubility of Lead Sulphate in Ammonium Acetate Solutions.

Since ammonium acetate is very hygroscopic, it is impracticable to obtain a solution of known strength by weighing out the salt. The solution was therefore prepared by the neutralisation of ammonium hydroxide with acetic acid. Pure ammonia, free from amines, was prepared by the following method (Bender u. Erdmann, "Preparationskunde," p. 234):—Commercial ammonium chloride, "free from hydrocarbons," was dissolved in enough boiling water to form a saturated solution. One-tenth of its volume of nitric acid (sp. gr. 1.42) was added, and the solution boiled until there was no further evolution of chlorine. The solution was then allowed to cool, the crystallised salt dissolved in water, one-twentieth of its volume of nitric acid added, and the solution again boiled as long as chlorine was given off. After diluting sufficiently to form a nearly saturated solution when cold, the salt was decomposed by lime. The ammonia was absorbed in conductivity water, carbon dioxide being carefully excluded by the use of soda-lime

tubes. The ammonium hydroxide solution so obtained was standardised with the help of methyl orange against a solution of pure hydrochloric acid, whose strength had been determined by precipitation with silver nitrate. An acetic acid solution was prepared by diluting glacial acetic acid with water. It was standardised with the help of phenolphthalein against the barium hydroxide solution, which had been titrated against the hydrochloric acid. The standardisations were made by weight, so as to give the number of grms. of acetic acid solution which were equivalent to 1 gm. of ammonium hydroxide solution. The neutral ammonium acetate solution was then prepared by adding to a given weight of the latter solution the appropriate weight of the former. Taking into account also the specific gravity of the two solutions, the concentration of the ammonium acetate solution so obtained was calculated to be 0.4141 equivalent per litre. The lead sulphate used was prepared by precipitating the commercial chemically pure lead acetate from solution by sulphuric acid, dissolving the precipitate in pure ammonium acetate, and re-precipitating with sulphuric acid.

For the determination of the lead dissolved in the ammonium acetate solution, two methods were tested by using known weights of pure lead sulphate. The first consisted in precipitation as lead chromate from acetic acid solution, filtering upon a Gooch crucible, and drying at 170°; the second in precipitation as lead sulphate by sulphuric acid, filtering upon a Gooch crucible, washing first with dilute sulphuric acid, and then with 50 per cent alcohol, and drying at 170°.

The former method gave results about 0.7 per cent too high, owing probably to the carrying-down of an excess of chromic acid; the latter method gave results which trial analyses showed to be accurate within 0.05 per cent.

The solutions were saturated by rotating the ammonium acetate solutions with a large excess of solid lead sulphate for fifteen hours within a thermostat at 25° in the manner previously described (Noyes, *Zeit. Phys. Chem.*, 1892, ix., 606). In half the determinations (marked s in the table below) the equilibrium was approached from the super-saturated side, by cooling a solution which had been shaken with the salt at a higher temperature, while in the other half (marked u in the table) it was approached from the undersaturated side, by heating the solution from the room temperature to 25°. It will be seen that the two procedures gave substantially identical results.

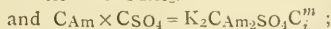
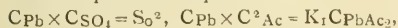
Table III. contains the results obtained, the solubility of the lead sulphate as well as the concentration of the ammonium acetate being expressed in the first three columns in millimols. per litre. In the fourth column the solubility in grms. per litre is added. For comparison, is included also the solubility in pure water, or rather the concentration of the ionised portion in the saturated solution in water, as determined by Böttger by conductivity measurements (*Zeit. Phys. Chem.*, 1903, xlv., 604).

TABLE III.—Solubility of Lead Sulphate in Ammonium Acetate Solutions at 25°.

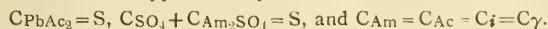
Concentration of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.	Separate determination.	Solubility of PbSO_4 .	
		Mean millimols. per litre.	Mean grms. per litre.
0.0	—	0.134	0.041
103.5	2.10 s	2.10	0.636
—	2.10 u		
207.1	4.54 s	4.55	1.38
—	4.56 u		
414.1	10.12 s	10.10	3.06
—	10.09 u		

It is seen from the table that the solubility is about fifteen times as great in 0.1 normal ammonium acetate solution as in water, and that it increases with increasing concentration of the salt somewhat, but not very much, more rapidly than proportionality between solubility and concentration would require.

It seems certain from the conductivity and migration experiments above described that this increase of the solubility is mainly due to the formation of un-ionised lead acetate, accompanied, of course, by the production of an equivalent quantity of ammonium sulphate, which would exist partly as ions and partly as un-ionised molecules. Assuming now that the solubility product, $C_{Pb} \times C_{SO_4}$, retains the same value as in pure water, the solubility in any ammonium acetate solution might be computed if it were possible to determine the resulting concentration of un-ionised lead acetate—a quantity which is substantially equivalent to that solubility. Unfortunately, however, our knowledge of the ionisation-relations, not only of lead acetate itself, but also in general of mixtures of salts which do not conform to the mass action law, is still very imperfect, and any assumption that may be made, especially with regard to the slightly ionised lead acetate, is arbitrary. Nevertheless, it is perhaps not without interest to determine whether the solubility-change with the concentration is satisfactorily explained if it be assumed that this salt follows the mass action law (which may well be true in virtue of its small ionisation tendency), and that ammonium sulphate follows the empirical law which has been shown to apply to mixtures of largely ionised salts (see Noyes, *Science*, 1904, xx., 577; *Tech. Quart.*, 1904, xvii., 293; *Journ. Am. Chem. Soc.*, xxvii., R, 203). We then have the the equilibrium equations:—



where S_0 is the solubility of lead sulphate in pure water, K_1 and K_2 are equilibrium-constants, m is an empirical exponent, and C_i is the total concentration of all the positive or negative ions in the solution. Furthermore, if S is the solubility of lead sulphate in a solution of ammonium acetate of concentration C and ionisation γ , the following relations given by the conditions of the problem also hold true approximately:—



Combining these equations, we get—

$$S = \frac{S_0}{\sqrt{K_1}} (C\gamma) \left(1 + \frac{1}{K_2} (C\gamma)^{1-m} \right)^{\frac{1}{2}}.$$

Now Kohlrausch's conductivity measurements at 18° with potassium sulphate, whose ionisation relations may be assumed identical with those of ammonium sulphate, show that $m = 0.59$ and $K_2 = 0.881$ when computed for the concentrations between 0.1 and 0.5 normal. The preceding equation therefore becomes—

$$S = \frac{S_0}{\sqrt{K_1}} C\gamma \left(1 + 1.135 (C\gamma)^{0.41} \right)^{\frac{1}{2}}.$$

It will be seen at once that this equation requires that the solubility increase a little more rapidly than the ionic concentration of the salt. By means of it the solubility at the two concentrations, 0.1036 and 0.414 molal can be computed from that in the 0.207 molal solution, the value of $S_0/\sqrt{K_1}$ being first calculated from the data for the latter. For these purposes we have obtained γ from the conductivity data of Kohlrausch at 18° for sodium acetate, whose ionisation relations doubtless correspond closely to those for ammonium acetate. We have thus calculated the solubility at the other two concentrations, and found it to be that shown in the following table. The concentrations of the ammonium acetate are here expressed in equivalents and those of the lead sulphate in millimols. per litre.

TABLE IV.—Observed and Calculated Solubilities of Lead Sulphate.

Concentration of $NH_4C_2H_3O_2$	Ionisation of $NH_4C_2H_3O_2$	Solubility of $PbSO_4$.	
		Observed.	Calculated.
0.1035	0.775	2.10	2.34
0.2071	0.724	4.55	—
0.4141	0.652	10.10	8.56

It will be seen that the change of solubility with the concentration is roughly, and only roughly, that required by the foregoing formula.

Finally, it may be mentioned that, to determine whether the requirement of the hypothesis is fulfilled, that sodium acetate has nearly the same effect on the solubility of lead sulphate as ammonium acetate, normal solutions of these two substances were shaken occasionally at room temperature for two days with an excess of solid lead sulphate, and a 100 c.c. portion of each was analysed for its lead-content. The ammonium acetate solution yielded 0.42 grm., and the sodium acetate solution 0.45 grm. of lead sulphate. These experiments were very rough ones, for the solutions were made up by weighing out the commercial "chemically pure" salts without thorough drying, the temperature was variable, and complete saturation may not have been reached. Still they certainly show that the two salts have, at least roughly, the same effect.

VI. Summary.

New measurements of the conductivity of lead acetate solutions at 25° between $\frac{1}{2}$ and $\frac{1}{15}$ -normal, have been presented, which show that this salt has an abnormally small degree of ionisation (only about 22 per cent at 0.1 normal, assuming that it dissociates directly into three ions).

Qualitative migration experiments made with a saturated solution of lead sulphate in normal ammonium acetate solution have been described, which show that the lead in this solution is not present to an appreciable extent in the form of either a positive or negative ion.

The solubility of lead sulphate (in millimols. per litre) has been found to be 2.1 in 0.104 normal ammonium acetate solution, 4.55 in 0.207 normal, and 10.1 in 0.414 normal. The solubility is very much greater than that in pure water (0.134 millimol. per litre according to Böttger), and is roughly proportional to the concentration of the ammonium acetate. Rough comparative experiments with sodium acetate and ammonium acetate showed that the solubility of lead sulphate in solutions of these two salts is of about the same magnitude.

These facts all indicate that the increased solubility of lead sulphate in acetate solutions arises mainly from the formation of un-ionised lead acetate by metathesis.

THE STUDY OF ABSORPTION SPECTRA IN RELATION TO THE CHEMICAL STRUCTURE OF COLOURLESS AND COLOURED SUBSTANCES.*

By WALTER NOEL HARTLEY, F.R.S.,
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THE hydrocarbons, unless of the benzene type, exert a continuous absorption of the ultra-violet rays, but the aromatic hydrocarbons commencing with the simplest in structure benzene exhibit spectra with absorption bands. Benzene exhibits different bands and bands differently situated, though evidently related, according to whether it is examined in the state of vapour or in solution in alcohol (Paur, *Wiedemann's Ann.*, 1891, lxi., 663; W. Friederichs, *Zeit. f. Wissenschaftliche Photographie*, 1905, iii., 154; also L. Grebe, iii., 376). When the substance is in a state of vapour there are differences corresponding—1st, to temperature, 2nd, to pressure, as well as to the thickness of the layer of vapour examined. The spectrum is a very complex one; no fewer than 91 narrow bands have been measured in my laboratory on one photograph taken from a column of air 12 c.m. long, saturated with benzene vapour at a temperature of 25° and 759.5 m.m. barometric pressure. When the hydrocarbon is in solution, the spectrum varies with the quantity of substance which the

* A Paper read at the Sixth International Congress of Applied Chemistry, Rome, April 27th, 1906.

rays traverse, or with the concentration of the solution. Working with instruments of small dispersion, such as the usual quartz spectrograph, there are eight bands or groups of bands in the spectrum of benzene dissolved in alcohol, six of which are seen to be of special importance, and of the six there are four which are not only better defined but more persistent or of greater intensity and breadth than the others, and they appear to be similarly constituted. A similar group of four bands occurs in the spectra of solutions of naphthalene, anthracene, and phenanthrene, but situated in less refrangible rays as the molecules are more complex, one of the bands of anthracene being in the violet. The spectrographic examination of organic products was first usefully applied in the study of essential oils, these being articles of great commercial value (Hartley and Huntington, *Proc. Roy. Soc.*, 1880). The hydroaromatic hydrocarbons and the camphors show spectra with different absorptive powers but without absorption bands, and of these thirty-five were examined. But from many essential oils, substances with a different constitution were separated which had a powerful absorption, and showed spectra with bands characteristic of the aromatic group. Thirteen samples of such substances showed that by diluting the original oils with alcohol the presence of bodies of the aromatic class could be detected, and in some cases the amount of these substances was estimated. Hydrocarbons derived from benzene by substitution of alkyl radicals for hydrogen exhibit modifications of the benzene spectrum in this respect, that several small bands are merged into one broad one, but, as a rule, two or three narrow bands are observed in the less refrangible part of the spectrum. Cymene is a good example of this, and by the absence of its bands it was concluded that its natural occurrence in essential oils is rare, though judging from its absorption spectrum, as much as four per cent was found in a Russian oil of turpentine. As it is easy to distinguish between aliphatic, hydroaromatic, and aromatic hydrocarbons, between alkylamines and aromatic bases, alcohols and phenols by their absorption spectra, and particularly by what I have described as the curves of molecular vibrations, so also isomeric substances of the aromatic group have different absorption curves which are invariably the same for the same pure substance. By comparing the curve of natural salicylic acid obtained from oil of wintergreen with the artificial product made by crystallising the calcium salt, the identity of the two products was established, and the pure commercial product was found to possess the properties now described as "physiologically pure." More recently the identity in constitution of phloroglucinol was established in specimens prepared from five different sources (Hartley, Dobbie, and Lauder, *Chem. Soc. Trans.*, 1902, lxxxii., 929).

Heterocyclic compounds and derivatives such as pyridine and quinoline, behave like the homocyclic rings, inasmuch as they show powerful absorption bands.

The application of the spectrographic method to the identification of the alkaloids, and for studying their constitution, has very clearly established its value. Thus the absorption spectra of a number of pure specimens were first photographed by the author; three years afterwards the same solutions were examined and compared with another series freshly prepared, the work being entrusted to an assistant, and a comparison of the two series of measurements of the spectra made independently showed no difference between them. Thirteen years later another collection of specimens was examined by Messrs. Dobbie and Lauder, and as their measurements agreed with the previous ones, there is shown to be no difficulty in identifying pure specimens. The action of different solvents, and of acids and bases on the alkaloids, may be very usefully employed in connection with the spectrograph, always provided that the use of nitric acid be excluded, because nitric acid itself yields an absorption band in the ultra-violet, whereas acetic, hydrochloric, and sulphuric acids do not. The absorption curves of the hydrochlorides differ somewhat from those of the bases, and some of them, such

as those of tertiary bases, are liable more or less to undergo hydrolysis. An important consideration in the spectrographic examination is the very small quantity of a substance required; most usually this is not more than a molecular weight in m.grms., or it may be only 0.1 gr. when the molecular weight of the substance is not known. The substance is not lost, but may be regained by evaporating the solvent after the solution has been used.

The following generalisations are of practical utility:—

If the absorption curve of a substance of which the composition and molecular weight are known, but the constitution is unknown, be compared with the curve of a similar substance the constitution of which has been ascertained, and if it be found that the difference between the curves amounts to no more than trifling differences in detail, it is right to assume that they both have the same structure.

Substances with the same formulæ giving widely different absorption curves or series of absorption spectra, are themselves structurally different.

Substances which, from their formulæ, are supposed to be homologous, are structurally different if their absorption curves differ widely.

Alkaloids which differ by CH_2 and are strictly homologous show curves which are practically identical.

Substances with the same molecular weight which give absorption curves which are identical, have the same structure, but if with the same structure they differ in optical properties, such as the rotation of a ray of polarised light, they are probably stereo-isomerides (Dobbie and Lauder, *Brit. Assoc. Report*, 1903).

Alkaloids which differ from one another simply by variations in the composition of side-chains, but not in that of the nucleus, show but slight alterations in their absorption curves.

Tautomerism.—In the study of tautomerism the absorption spectra are most valuable, because nothing but the solvent need come into contact with the substance to be examined, and the effect of different solvents may be studied, but in all such cases experience has shown that it is advisable to avoid the application of heat for the purpose of facilitating solution, and also to photograph the spectra as soon as possible after the solution has been prepared, otherwise desmotropic changes may spontaneously take place. The action of heat is capable of causing such changes rapidly, which, at ordinary temperatures, require days, or even weeks, for their completion. Cotarnine is an example of an alkaloid which Dobbie, Lauder, and Tinkler (*Chem. Soc. Trans.*, 1904, lxxxv., 121) have shown exists in two isomeric states, according to whether it is dissolved in ether or alcohol. Brühl has shown that a comparison of the physical properties of benzene—namely, its density, its refraction equivalent, its molecular volume at 20°C ., its specific dispersion, molecular refraction, and molecular dispersion—with the similar properties of dihydrobenzene, tetrahydrobenzene, hexahydrobenzene, hexane, hexylene, diallyl, and dipropargyle, presents a complete substantiation of the formula by which Kekulé represented the special chemical properties of benzene as being a consequence of its constitution (*Ann. Chem. Pharm.*, clxii., 86). This conclusion has also been confirmed by its absorption spectrum and that of its derivatives. Furthermore, von Baeyer has obtained chemical evidence of the benzene nucleus existing in two different states which are to be considered as tautomeric; the difference between them being due to a different linking of the carbon atoms within the molecule, but not to any change in the position of the hydrogen atoms. It has been termed phaseotropy by Laar (*Ber.*, 1901, xxiv., 3516). This also agrees with Kekulé's view, and is also in harmony with recent work on absorption spectra. To consider this subject in all its bearings, it is necessary to take into account the relationship of certain colourless compounds to the coloured derivatives obtained from them. The curves of molecular vibrations of benzene, triphenyl methane and the dyes derived from them, and similarly benzene, azo-benzene, and

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END OF VOLUME XCHII.

the azo-dyes afford evidence of the physical relationship of the colourless to the coloured compounds (*Chem. Soc. Trans.*, 1887, li., 153).

Murexide was the only purely organic colouring matter of approximately ascertained constitution at that time which was not derived from benzene. To account for the absorption band in uric acid, and the colour developed in murexide, it was stated that it apparently depended upon a peculiar linking of the CO and N groups in these compounds. Since 1887 we have become acquainted with several others, such as the unsaturated ketones (O. Wallach, *Chem. Central.*, 1897, i., 373), ethylnitrolic acid, and violuric acid which yield coloured salts and coloured solutions. The chromogenic properties of these acid-forming substances have been accounted for by the simultaneous operation of a physico-chemical change and a purely chemical one, both of which are included in the term ionisation isomerism (A. Hantzsch, *Ber.*, 1899, xxxii., 575, also 307; J. Guinard, *Ber.*, 1899, xxxii., 1723). Messrs. Bier and Marchlewski have drawn attention to the fact that atomic groupings are apparently the cause of a band or bands in the absorption spectra of certain compounds and not the nucleus of the compound simply, as in benzene and triphenylmethane and its derivatives (*Extrait du Bull. Acad. des Sciences de Cracovie*, April, 1902), and in this connection a spectrographic and chemical examination of uric acid, the ureides, and murexide has placed us in possession of the following facts (*Chem. Soc. Trans.* 1905, lxxvii., 1791—1831).

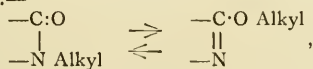
Urea and the ureides, alloxan, barbituric acid, dialuric acid, alloxanic acid, potassium alloxanate, pure violuric acid, uramil, and guanine hydrochloride show no absorption band or bands in their spectra, and as a rule they transmit the ultra-violet rays very freely. These oximino-rings have the same optical properties as cyanuric acid and its esters, tricarbamide and its esters, melamine and its triethyl esters, also diketohexamethylene (*Brit. Assoc. Report*, 1901, Hartley, Dobbie, and Lauder). Substances which show bands in their absorption spectra, or in which bands may be developed by a tautomeric change are—(a) certain oxypurin derivatives, and (b) diureides, or substances which contain two oximino-rings linked together by oxygen or by nitrogen. The substances referred to are uric acid and alkali urates, alkali violurates, caffeine, theobromine, ethoxy-caffeine, and alloxantin. In order to determine whether any particular structural differences occur in the constitution of those substances which exhibit absorption bands and those which do not, their properties were carefully examined and compared.

First, a ring structure is not essential, since simple oximino-ketone rings show no bands.

Secondly, the oxypurin compounds which show bands in their spectra are easily converted into simple oximino-ketones which do not.

Thirdly, the unsaturated ketones, some of which are open chain compounds, have ethylenic linkings associated with a carbonyl group (C:O), which arrangement is apparently the cause of their colour.

Fourthly, by methylating oxycaffeine, E. Fischer obtained the ketonic and enolic isomerides, tetra-methyluric acid, and methoxycaffeine. W. Wislicenus and Körber found (*Ber.*, 1902, xxxv., 1992), by continued heating, ethoxy-caffeine is converted into trimethyluric acid. These changes reduced to their simplest expression may be represented thus:—



where the conversion of the ketonic into the enolic form causes a double linking (C:O) external to the ring, to be changed to a double linking within the ring. Spectrographic observations have also revealed the fact that these tautomeric changes do take place in some of the oxypurin derivatives, and that they are liable to occur in ali, and are accelerated by heat.

Guanine hydrochloride which shows no band, contains three double linkings in a ring structure, but the other five purin compounds contain but two; it is obviously not the three ethylenic linkings which cause the band, but the number and disposition of the ketone complexes, with respect to double linking, which admits of the change

$\text{·NH>CO} \rightarrow \text{·N}\equiv\text{C·OH}$ in the 2:6:8- and 2:6-oxy-purins, with the simultaneous double linking within the ring when the ketonic passes into the enolic form. The diureide alloxantin in aqueous solution shows a band which afterwards disappears by reason of the substance being hydrolysed into dialuric acid and alloxan.

Fifthly, it may be pointed out that the alkali and alkaline earth metals induce the formation of a band in certain compounds, and intensify it where it is already existent; they also produce colour.

A similar action is to be attributed to aluminium hydroxide in its effect on acetylacetone and ethylacetoacetate. Baly and Desch attribute the formation of a band in the spectrum of acetylacetone not solely to one structure, or another which it is possible to formulate for the same substance, but to the change from the one to the other structure (*Chem. Soc. Trans.*, 1904, lxxxv., 1029). Now colour has been cited by T. M. Lowry as evidence of isodynamic change, since nearly all coloured substances can be re-prepared by two formulæ (*Brit. Assoc. Report*, Cambridge, 1904, pp. 193—224). The terms *dynamic isomerism* and *tautomerism*, though applied to the same class of phenomena, are not identical in meaning. *Dynamic isomerism* implies a state of equilibrium between two or more isomeric forms in different molecules of the same compound. By *tautomerism* it must be understood that, the oscillation of a hydrogen atom between two positions in the one molecule endows the molecule with a different structure at each phase of the vibration, so that it possesses the properties alternately of two isomeric forms. This is strictly a reversible isomerism. Equilibrium between isomers in many cases is possible only in presence of a third substance, which may be a minute trace of impurity. Equilibrium may be affected by the solvent, concentration, and temperature. By assembling and collating the foregoing facts and theories we arrived at the following generalisation:—

In benzenoid hydrocarbons, oximino-, or ketonic compounds, the occurrence of a banded spectrum results from either phaseotropy, isodynamic change, or tautomeric change; and for the isodynamic or tautomeric change to become possible, a certain peculiarity in structure is necessary.

(To be continued).

ELECTRO-CHEMICAL CALCULATIONS.*

By JOSEPH W. RICHARDS.

(Concluded from p. 21).

POTENTIAL FOR MIXED ELECTROLYSIS.

THE above data are easily applied when the current is doing only one thing, i.e., is separating out or dissolving only one element. But in many cases the current is causing a compound anode to dissolve, as when copper and silver both dissolve from a silver bullion anode; or two or more metals may be simultaneously deposited, as when copper and zinc are deposited together as brass. In all such cases, the simplest procedure is to foot up the thermochemical energy of the total electro-chemical change for any given time or number of coulombs passing. Then express this per 96,540 coulombs passing, and divide by 23,040; the quotient will be V_d .

$$\text{Voltage drop (V}_d\text{)} = \frac{Q \text{ for 96,540 coulombs passing}}{23,040}$$

* From the *Journal Franklin Institute*, February and March, 1906.

Example.—An electrolyte contains zinc sulphate with some copper sulphate, and is electrolysed with a copper anode. There is deposited upon the cathode in one hour 15 grms. of brass, containing one-third zinc and two-thirds copper. What voltage drop will occur in the cell in addition to that necessary to overcome its ohmic resistance?

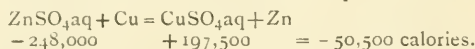
Solution.—The coulombs passing are those necessary to deposit 5 grms. of zinc (chemical equivalent, $65 \div 2$) and 10 grms. of copper (chemical equivalent $63.6 \div 2$).

$$\begin{aligned}\text{Coulombs for zinc} &= \frac{5 \cdot 0000}{0 \cdot 00001035 \times (65 \div 2)} = 14,864 \\ \text{Coulombs for copper} &= \frac{10 \cdot 0000}{0 \cdot 00001035 \times (63 \cdot 6 \div 2)} = 30,383 \\ \text{Sum} &= 45,247\end{aligned}$$

The weight of copper dissolved will be, on the same principles,—

$$45,247 \times 0 \cdot 00001035 \times (63 \cdot 6 \div 2) = 14 \cdot 892 \text{ grms.}$$

The solution of 14.892 grms. of copper and deposition of 10 grms. of the same element, shows that the only thermo-chemical energy required is that absorbed for the solution of 4.892 grms. of copper, and deposition therefore of 5.0 grms. of zinc. The thermo-chemical equation is—



Showing that 50,500 calories is absorbed for every 65 grms. of zinc (its atomic weight) thus deposited. This equals an absorption of 3885 calories per 5 grms. of zinc, or for the whole period, during which 45,247 coulombs passed through the cell. For every 96,540 coulombs passing, the thermo-chemical heat absorption is—

$$\frac{3,885}{45,247 + 96,450} = 8289 \text{ calories,}$$

and the voltage drop is—

$$\nabla d = \frac{8,289}{23,040} = 0 \cdot 36 \text{ volt.}$$

The above calculation is on the assumption that the copper and zinc deposit separately, as mixed crystals. If they really deposit as a chemical combination, the heat of formation of the alloy would need to be considered also in the above calculation.

The main point sought to be emphasised by the foregoing statements and illustration is that the current may, and very often does, do two kinds of chemical work simultaneously, requiring, if each alone took place separately, different drops of potential to accomplish the chemical work; in such cases, the only safe ground is to say that the coulombs passing must furnish the sum total of all the energy for all the chemical changes induced at the electrode surface, and therefore must drop sufficiently in potential to furnish the energy required (in addition, of course, to the ordinary drop of potential caused by the ohmic resistance of the bath).

CURRENT FOR MIXED ELECTROLYSIS.

When the current is dissolving or depositing only one element, the calculation of the quantity of material concerned with a given transfer of electricity is a simple question:—The Faraday, 96,540 coulombs, dissolves or deposits one chemical equivalent weight in grms.

If, however, two or more elements are simultaneously dissolved or deposited, as occurs frequently in metal refining or plating, the calculation is not so simple. The proper procedure in that case is to find how many coulombs are required for the separate weights of each element dissolved or deposited, and add these together to obtain the total current needed. Or, if the current used is given, and the question is the amounts of mixed metals dissolved or deposited, obtain the coulombs necessary to dissolve or

deposit 1 kilogram. of the alloy or mixed metals, and divide this into the total coulombs used.

Example.—In the Wohlwill process of refining gold bullion, the anodes consist of 80 per cent gold, 8 per cent silver, 10 per cent copper, and 2 per cent platinum. One hundred and fifty ampères pass through each cell, attacking or corroding the anodes uniformly, while the silver deposits at the bottom of the bath as AgCl, gold is deposited pure on the cathodes, and platinum and copper accumulate in the solution as PtCl₄ and CuCl₂ respectively.

Required.—1. How much weight of anode is corroded per twenty-four hours?

2. How much more gold is deposited than is dissolved?

3. What voltage of decomposition, to represent chemical work, must be furnished?

Solution.—1. One kilogram. of anode contains—

Gold	..	..	..	..	..	800	grms.
Silver	..	..	..	..	..	80	"
Copper	..	..	..	..	..	100	"
Platinum	..	..	..	..	..	20	"

The coulombs necessary to dissolve these weights and to convert these metals into AuCl₃, AgCl, CuCl₂, and PtCl₄ are:—

		Coulombs.
Gold	..	800 $\div$ ($0 \cdot 00001035 \times 197 \div 3$) = 1,177,076
Silver	..	80 $\div$ ($0 \cdot 00001035 \times 108 \div 1$) = 71,570
Copper	..	100 $\div$ ($0 \cdot 00001035 \times 63 \cdot 6 \div 2$) = 303,831
Platinum	..	20 $\div$ ($0 \cdot 00001035 \times 195 \div 4$) = 39,638

1,592,115

Coulombs available per twenty-four hours—

$$150 \times 60 \times 60 \times 24 = 12,970,000.$$

Anode corroded away in twenty-four hours, per cell—

$$\frac{12,970,000 \div 1,592,115 = 8 \cdot 146 \text{ kilograms.}}{= 8,146 \text{ grms.}} \quad (1)$$

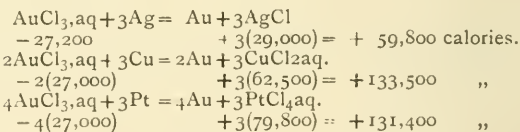
2. The weight of gold deposited, by the total current, is

$$\frac{12,970,000 \times (0 \cdot 00001035 \times 197 \div 3) = 8815 \text{ grms.}}{\text{Amount dissolved, } 8146 \times 0 \cdot 80 = 6717 \text{ "}}$$

$$\text{Shortage in each cell, per 24 hours} = 2098 \text{ " } \quad (2)$$

This shortage, it will be recalled, has to be made up by dissolving some of the bullion in acid, and adding to the cells. There would be required $2098 \div 0 \cdot 80 = 2747$ grms. of bullion thus dissolved, making the total bullion treated per cell per day $8146 + 2747 = 10,893$ grms., of which 8146 grms. or 74.8 per cent would be treated electrolytically in the cell, and the rest, 25.2 per cent, would be dissolved chemically, and yet when added to the electrolyte, its gold deposited electrically.

3. Basing calculations on the solution of a kilogram. of anode, requiring the passage of 1,592,115 coulombs (16.49 Faradays), the 800 grms. of gold dissolved has a corresponding 800 grms. deposited, so that no chemical energy needs to be expended for it. For the other elements we have the following equations and heat absorptions or evolutions:—



The above heat evolutions are for the solution of, respectively,—

3 grms. atomic weights of silver	= 324 grms.
3 " " " copper	= 190.8 " "
3 " " " platinum	= 585.0 " "

The heat evolution per kilogram. of anode corroded will therefore be for:—

80 grains silver	=	$\frac{80}{324} \times 59,800$	= 14,765 calories
100 " copper	=	$\frac{100}{190.8} \times 133,500$	= 69,980 "
20 " platinum	=	$\frac{20}{585} \times 131,400$	= 450 "
Sum = 85,195 "			

This heat evolution takes place for the passage of 1,592,115 coulombs (16.46 Faradays). For one Faraday (96,540 coulombs) it will be,—

$$85,195 \div 16.49 = 5167 \text{ calories,}$$

and since one Faraday falling in potential one volt represents 23,040 calories, the heat evolution will generate—

$$5167 \div 23,040 = 0.224 \text{ volts,}$$

which means that the fall of potential for chemical work is negative, i.e.,

$$V_d = -0.224 \text{ volts} \quad \dots (3)$$

It is interesting to note that, the observed total drop of potential across the baths being 0.7 volt, the voltage drop to overcome ohmic resistance must be greater than this, i.e.,

$$V = V_d + V_c$$

$$0.7 = -0.224 + V_c$$

$$V_c = 0.7 + 0.224 = 0.924 \text{ volt,}$$

making the ohmic resistance of the cell—

$$R = \frac{0.924}{150} = 0.00616 \text{ ohms}$$

$$= 6.16 \text{ milli-ohms.}$$

Further, if no external source of current were used, the cell would have available 0.224 volt electromotive force, which should, if short circuited, send—

$$0.224 = 36.3 \text{ ampères}$$

$$0.00616$$

through the bath; that is, run it at 24 per cent of the present rate, without any external generator of current.

RISE IN TEMPERATURE OF BATHS.

A subject of much importance is that of the temperature of an electrolytic cell being maintained above the room temperature by the heating effect of the current. It is difficult to calculate ahead, before the apparatus is constructed, how high its temperature will rise above its surroundings, but it may be determined with considerable approach to accuracy how high it will be heated as soon as it has been constructed, and before electric current is applied, by a simple test.

The tank is filled with electrolyte, the electrodes put in place, and note made of the weight of electrodes and electrolyte. The tank is heated by a steam-pipe until at desired temperature above the room, and then allowed to cool by radiation, with thermometer immersed in the electrolyte so as to determine the rate of fall of temperature per minute. An ordinary tank will cool approximately twice as fast if uncovered as if covered. Tests on a small tank showed, for example, the following results:—

At 90° C. falling 3.2° per minute.

" 80°	"	1.7°	"
" 70°	"	1.1°	"
" 60°	"	1.0°	"

Knowing the weight and heat capacity of the electrodes and electrolyte (to which may be added half the heat value of the tank), it can be calculated how much heat is being lost per minute at any of the above temperatures. To maintain the bath at that temperature would therefore require just that much heat to be generated within it electrically in overcoming the ohmic resistance, and if we know or have calculated the electric resistance of the bath we have,—

$$\text{Heat generated in bath} = (\text{current used})^2 \times \text{resistance} \times 0.2385 \text{ calories per second,}$$

and therefore the current required to supply any required quantity of grm.-calories per minute will be,—

$$\text{Current} = \sqrt{\frac{\text{Heat to be generated in bath per minute}}{\text{Resistance of bath in ohms} \times 0.2385 \times 60}}$$

This same method of investigation can be applied to apparatus working with fused salts, or electric furnaces, providing that means of measuring the temperature satisfactorily are at hand.

ENERGY REQUIRED FOR CHEMICAL WORK.

This energy must be equal in amount to the chemical work done, and the only measure of this that we have are the thermo-chemical heats of combination of the separated-out products to reform the original material. A most striking generalisation has been arrived at by the discussion of thermo-chemical data, viz., that taking the heats of formation of salts plus their heat of solution in excess of water (usually called "heat of formation to dilute solution"), these quantities are found to be additive in their nature, such being composed of the sum of two quantities, one characteristic once for all of the base, in all its combinations, and the other being characteristic once for all of the acid radical, in all of its combinations. There is thus for each basic element a *thermo-chemical constant*, which represents the amount of heat it contributes to the formation-heat of a salt, the latter taken in dilute solution; and for each acid radical a similar *thermo-chemical constant*, representing in a similar manner the part which it contributes; the sum of these two

TABLE I.—Thermo-chemical Constants of Basic Elements.

	Per chemical equivalent.	Corresponding voltage.
	Calories.	
Li'	+62,900	+2.73
Rb'	62,000	2.69
K'	61,900	2.69
Ba'	59,950	2.60
Sr'	58,700	2.55
Na'	57,200	2.48
Ca'	54,400	2.36
Mg'	54,300	2.36
Al'	40,100	1.74
(N + H ₄)' ..	33,400	1.45
Mn'	24,900	1.08
Zn'	17,200	0.75
Fe'	10,900	0.47
Cd'	9,000	0.39
Co'	8,200	0.36
Ni'	7,700	0.33
Fe'	3,230	0.14
Sn'	1,900	0.08
Pb'	400	0.02
H'	0	0
Th'	-900	-0.04
Cu'	-7,900	-0.34
Hg'	-14,250	-0.62
Pt'	-19,450	-0.84
Ag'	-25,200	-1.10
Au'	-30,300	-1.32

TABLE II.—Thermo-chemical Constants of Acid Elements.

	Per chemical equivalent.	Corresponding voltage.	Salt.
F ₂ ' (gas)	+52,900	+2.30	Fluoride
Cl ₂ ' (gas)	39,400	1.71	Chloride
Br ₂ ' (gas)	32,300	1.40	Bromide
Br' (liquid)	28,600	1.20	Bromide
Br' (solid)	27,300	1.18	Bromide
I ₂ ' (gas)	20,000	0.87	Iodide
I' (liquid)	14,600	0.63	Iodide
I' (solid)	13,200	0.57	Iodide
S' (solid)	-5,100	-0.22	Sulphide
Se' (met.)	-17,900	-0.78	Selenide

TABLE III.—Thermo-chemical Constants of Acid Radicals. (From their Elements).

Constituents.	Radical.	Per chemical equivalent.	Corresponding voltage.	Salts.
O ₂ (gas), H ₂ (gas)	(OH)'	+55,200	+2.40	Hydrate
S(solid), H ₂ (gas)	(SH)'	3,400	0.15	Sulphhydrate
Se(met.), H ₂ (gas)	(SeH)'	19,100	0.83	Selenhydrate
Cl ₂ (gas), O ₂ (gas)	(ClO)'	27,500	1.19	Hypochlorite
Cl ₂ (gas), O ₂ (gas)	(ClO ₂)'	21,900	0.95	Chlorate
Cl ₂ (gas), O ₂ (gas)	(ClO ₃)'	39,400	1.71	Perchlorate
Br ₂ (gas), O ₂ (gas)	(BrO)'	28,600	1.24	Hypobromite
Br ₂ (gas), O ₂ (gas)	(BrO ₂)'	12,500	0.54	Bromate
I(gas), O ₂ (gas)	(IO ₃)'	65,000	2.82	Iodate
I(gas), O ₂ (gas)	(IO ₄)'	52,600	2.28	Periodate
S(solid), O ₂ (gas)	(S ₂ O ₃)''	71,750	3.11	Hyposulphite
S(solid), O ₂ (gas)	(SO ₃)''	75,100	3.26	Sulphite
H ₂ (gas), S(solid), O ₂ (gas)	(HSO ₃)'	149,400	6.48	Bisulphite
S(solid), O ₂ (gas)	(S ₂ O ₅)''	115,200	5.00	Pyrosulphite
S(solid), O ₂ (gas)	(SO ₄)''	107,000	4.64	Sulphate
H ₂ (gas), S(solid), O ₂ (gas)	(HSO ₄)'	211,100	9.16	Bisulphate
S(solid), O ₂ (gas)	(S ₂ O ₈)''	158,100	6.86	Persulphate
S(solid), O ₂ (gas)	(S ₂ O ₆)''	138,500	6.01	Dithionate
S(solid), O ₂ (gas)	(S ₃ O ₆)'	136,500	5.92	Trithionate
S(solid), O ₂ (gas)	(S ₄ O ₆)''	130,600	5.67	Tetrathionate
S(solid), O ₂ (gas)	(S ₅ O ₆)''	133,100	5.78	Pentathionate
Se(solid), O ₂ (gas)	(SeO ₃)'	60,050	2.61	Selenite
Se(solid), O ₂ (gas)	(SeO ₄)''	72,800	3.16	Selenate
P(solid), O ₂ (gas)	(PO ₄)'''	99,300	4.31	Phosphate
H ₂ (gas), P(solid), O ₂ (gas)	(HPO ₄)''	152,750	6.63	Mono-H-phosphate
H ₂ (gas), P(solid), O ₂ (gas)	(H ₂ PO ₄)'	307,700	13.35	Di-H-phosphate
As(solid), O ₂ (gas)	(AsO ₂)''	102,150	4.43	Arsenite
As(solid), O ₂ (gas)	(AsO ₄)'''	70,200	3.05	Arsenate
H ₂ (gas), As(solid), O ₂ (gas)	(HASO ₄)''	71,700	3.11	Mono-H-arsenate
H ₂ (gas), As(solid), O ₂ (gas)	(H ₂ AsO ₄)'	217,200	9.43	Di-H-arsenate
N ₂ (gas), O ₂ (gas)	(NO ₃)'	48,800	2.12	Nitrate
N ₂ (gas), O ₂ (gas)	(NO ₂)'	27,000	1.17	Nitrite
N ₂ (gas), O ₂ (gas)	(NO)'	-3,800	-0.16	Hyponitrite
C(amor.), O ₂ (gas)	(C ₂ O ₃)''	99,800	4.33	Oxalate
C(amor.), O ₂ (gas)	(CO ₃)''	82,450	3.58	Carbonate
H ₂ (gas), C(amor.), O ₂ (gas)	(HCO ₃)'	169,100	7.34	Bicarbonate
H ₂ (gas), C(amor.), O ₂ (gas)	(CHO ₂)''	104,600	4.54	Formate
H ₂ (gas), C(amor.), O ₂ (gas)	(C ₂ H ₃ O ₂)''	120,500	5.23	Acetate
N ₂ (gas), C(amor.), O ₂ (gas)	(CNO)'	37,100	1.61	Cyanate
C(amor.), N ₂ (gas)	(CN)'	-34,900	-1.51	Cyanide
S(solid), C(amor.), N ₂ (gas)	(CNS)'	-18,100	-0.79	Sulphocyanide
Fe(solid), C(amor.), N ₂ (gas)	(FeC ₆ N ₆)'''	-25,600	-1.11	Ferrocyanide
Fe(solid), C(amor.), N ₂ (gas)	(FeC ₆ N ₆)'''	-52,800	-2.29	Ferricyanide

thermo-chemical constants is the formation heat of the salt, from its elements, to dilute solution. The thermo-chemical constant is nothing more nor less, in the case of a base, than *energy drop* which represents the decrease of free energy in the element as it passes from the free, uncombined state into the combined state in dilute solution; in the case of an acid element, the statement is entirely similar; in the case of an acid (or basic) radical, it is the total energy drop from free elements to the state of combination as a radical.

The arbitrary basis selected to which to refer these thermo-chemical constants is best that of hydrogen constant equal to zero. This would make the thermo-chemical constant of every basic element the heat evolved when it displaces hydrogen from a dilute solution of acid; and that of an acid element or radical the heat of formation of the corresponding acid in dilute solution. Practically, the thermo-chemical constants have been evaluated by the comparison of the heats of formation of many acids and salts, and the selection of the most probable experimental values. Tables I., II., and III. have been thus derived by the writer from an extensive discussion of the subject-matter. The constants are given in every case *per one chemical equivalent* for the base or acid, element or radical, and *not* for the normal number of equivalents which are designated by the symbol and dots (·) or accents (').

I have also given the voltage drop corresponding to an

energy drop of the designated number of calories per chemical equivalent, by the simple procedure of dividing the latter by 23,040.

In using these tables, it must be borne in mind that the sum of the thermo-chemical constants for the basic and acid constituents of any salt, gives the heat of formation of the salt from the constituent chemical *elements*, in dilute solution. Conversely, the heat of formation thus obtained is the energy necessary to separate the salt in dilute solution into its constituent chemical elements. The sum of the voltages, corresponding to this amount of chemical energy, is the voltage necessary to decompose the salt in solution into its constituent, free chemical elements. If these elements re-combine in the process of decomposition, to form other chemical compounds, then the whole chemical reaction must be taken into account—best on the total energy basis; and when this is expressed in calories per chemical equivalent concerned, the necessary voltage for producing the change is obtained by dividing this by 23,040.

Jubilee of the Coal-tar Colour Industry.—A meeting will be held in the Theatre of the Royal Institution, Albemarle Street, Piccadilly, on Thursday, July 26, at 11 a.m. All chemists are invited.

PROCEEDINGS OF SOCIETIES.

FARADAY SOCIETY.

Ordinary Meeting, July 2nd, 1906.

Prof. SILVANUS P. THOMPSON, D.Sc., F.R.S., in the Chair.

Prof. KR. BIRKELAND, of the University of Christiania, read a paper on "*The Oxidation of Atmospheric Nitrogen in Electric Arcs.*"

The paper deals principally with recent developments of the Birkeland-Eyde process for the fixation of atmospheric nitrogen as carried out in the nitrate manufactory at Notodden and at the experimental works at Arendal.

By way of introduction extracts are given from the Presidential Address delivered before the British Association in 1898 by Sir William Crookes, showing the urgent importance of the subject in consideration of the rapid rate of exhaustion of the world's present stock of fixed nitrogen—the great fertiliser for wheat—and it is pointed out that out of the air over each square mile of the earth's surface more saltpetre can be made than is to be found in the whole of Chili. A brief history of the oxidation of nitrogen by means of electricity includes references to the pioneering work of Priestley and Cavendish (about 1780), to the more recent work of Spottiswoode and Dewar (1880), Crookes (1892), and Rayleigh and Ramsay (1897), and finally to the technical applications developed by Bradley and Lovejoy (1903), and by Kowalski and Moscicki (1904).

The essence of the electrical side of the problem consists in the production of a stable and practical form of high-tension arc in which to effect the oxidation. This the author produces by placing an alternate current arc equatorially between the poles of a powerful electromagnet. The arc thus formed moves across the electric field with enormous velocity, while its length, and thus its resistance, increases so that the tension is heightened until a new arc forms at the points of the electrodes, and the long outer arc is extinguished. The positive and negative arcs move in opposite directions, and in this way a complete, luminous, circular disc of flame is formed. When the proper conditions are attained, and the arc is stable, one arc only, as shown by oscillograph records, is formed at each reversal of the current. The potential employed is 5000 volts, and the frequency 50. The electrodes, which are 8 m.m. to 1 c.m. apart, are made of copper tubing 15 m.m. in diameter, and are water-cooled; 7·5 per cent of the energy is wasted in this way as heat. The electrodes are removed for repair every three hundred hours.

The disc-flame is enclosed in a special furnace, which is described in the paper. The fire-chamber of this is only 5·15 c.m. wide, and air is driven into the central region by a Root's blower. At Notodden there are three such furnaces, each employing 500 kilowatts. In the new 30,000 H.P. plant, now in course of erection, the furnaces will each absorb from 750 to 850 kilowatts. Figures showing cost of erection and upkeep are given.

The air (75,000 litres per minute at Notodden), which after passing through the furnaces contains about 1 per cent of nitric oxide, discharges its superfluous heat into a steam-boiler, cooling from 700° C. to 200° C., and, finally, at 50° C. it enters the oxidation chambers in which the nitric oxide becomes nitric peroxide. It then passes to the absorption towers to be dissolved in water, forming, finally, 50 per cent nitric acid. The unabsorbed nitric fumes are converted into a fifth, milk-of-lime, tower to calcium nitrite and nitrate, which in turn is completely oxidised to nitrate by means of nitric acid. This nitrate lye, mixed with the bulk of nitric acid, reacts on limestone, and is converted into a solution of neutral calcium nitrate, which may be crystallised out either in the normal or basic form. The yield of the furnaces is given as 500 kilogrms. of anhydrous nitric acid per kilowatt-year, but this is a minimum yield. The inclusive cost of production is stated to be £4 a ton, the selling price being £8 a ton; at Notodden about 25s.

per E.H.P.-year is paid for power, but the cost is less than half of that.

The author finally discusses the theory of the oxidation of nitrogen in electric arcs, and incidentally he describes experiments made to determine the thickness of the arc threads. According to the simple thermo-chemical theory at every temperature a definite amount of NO is in equilibrium with a fixed mixture of air and nitrogen; at 3000° C., for example, an entire 5 per cent will be nitric oxide. To retain this quantity at a lower temperature the cooling must take place with very great rapidity. The great difficulty in making theoretical calculations is that of knowing the temperature of the arc. The author compares results obtained during a very careful trial run at Arendal with those calculated from Nernst's formula, assuming various temperatures for the arc, and he finally, after allowing for the length of time the maximum temperature is effective, assumes an average temperature of 3200° C. A higher temperature should be arrived at in practice, for the maximum theoretical output coincides with about 5200° C. The paper concludes with an estimate of the number of molecules in the arc that are split up into ions, and suggests comparisons with air ionised by means of radium. It may be that the proportion of gas ionised will be of determinative importance to the chemical equilibrium of gas compounds.

Dr. H. BURNS asked for further information relating to the absorption of the combined gases.

Dr. R. S. HUTTON discussed the figures given relating to power consumption. In reply, the author stated that less than 0·7 per cent of the total energy was absorbed in the magnets, and that in the new works only about 3 per cent of the total power would be used for auxiliary purposes outside the furnaces.

In reply to Dr. R. M. WALMSLEY, the author stated that greater efficiencies than 179 grms. per kilowatt-hour had been obtained recently.

Dr. O. J. STEINHART referred to the low cost of water-power given by the author. In reply, it was stated that the power at Notodden for which 25s. per E.H.P.-year was paid cost only 11s.

In reply to Dr. F. M. PERKIN, it was stated that the flow of gas cannot exceed a certain amount, or the flame would be extinguished.

The CHAIRMAN described the careful and elaborate trial to which the process had been put by the Commission referred to in the paper, and which entirely confirmed the claims made by the inventors regarding efficiencies and costs. He alluded to the well-known important work of Prof. Birkeland on the aurora borealis, and on the action of magnetic fields on cathode discharges, and showed how these purely scientific investigations led up to the working out of the present important industrial purposes.

Dr. EUGENE HAANEL, of the Department of the Interior, Ottawa, presented a "*Preliminary Report on the Experiments made at Sault Ste. Marie, under Government Auspices, on the Smelting of Canadian Iron Ores by the Electro-thermic Process.*" The paper was communicated by Mr. F. W. Harbord, F.I.C.

The experiments described were made for the purpose of amplifying the results obtained at La Praz and Livet by the Canadian Commission in 1904, in view of the special conditions obtaining in Canada.

The furnace, which is fully described and illustrated, was of the Héroult type; it absorbed 5000 ampères at 35 to 40 volts (power factor 0·919), being fed from a transformer of 225 kilowatt capacity. The official experiments, of which a selected number are explained in detail with full chemical, electrical, and thermal data, lasted nearly two months, and during that time 150 casts were made, yielding 55 tons of pig-iron. The experiments indicated that under normal conditions about 11·5 tons were produced by an expenditure of 1000 E.H.P.-days: with an improved furnace of, say, 1500 E.H.P. capacity, a figure of 12 tons should, it is stated, be reached. The mean figure provisionally adopted by the Commission was only

7·8 tons per 1000 E.H.P.-days. The consumption of electrode was about 18 lbs. per ton of pig-iron; it was greater for white than for grey iron.

The results obtained are summarised as follows:—

1. Magnetite (which is the chief Canadian ore) can be as economically smelted by the electro-thermic process as hematite.
2. Ores of high sulphur content not containing manganese can be made into pig-iron containing only a few thousandths of 1 per cent of sulphur.
3. The silicon content can be varied as required for the class of pig to be produced.
4. Charcoal, which can be cheaply produced from mill refuse or wood which could not otherwise be utilised, can be substituted for coke as a reducing agent, without being briquetted with the ore.
5. A ferro-nickel pig can be produced practically free from sulphur and of fine quality from roasted nickeliferous pyrrhotite.
6. The experiment made with a titaniferous iron ore containing 17·82 per cent of titanic acid permits the conclusion that titaniferous iron ores up to perhaps 5 per cent titanic acid can be successfully treated by the electric process.

The paper concludes with an estimate of Dr. Héroult for a 10,000 H.P. plant capable of producing 120 tons of pig-iron in twenty-four hours.

A paper on "*Electrolysis of Dilute Solutions of Acids and Alkalis at Low Potentials: Dissolving of Platinum at the Anode by a Direct Current*," by GEORGE SENTER, Ph.D., was taken as read.

When dilute solutions of sulphuric acid and of sodium hydroxide are submitted to electrolysis at a potential below that at which oxygen is evolved in the gaseous form, an oxidising agent is formed in very small amount at the anode. The substance is very stable, and is not destroyed by boiling; it is not hydrogen peroxide.

In the course of the experiments with dilute sulphuric acid, it was observed that traces of platinum went into solution from the anode, although the average current density was only about $1·5 \times 10^{-2}$ ampères per sq. c.m.; the bearing of this result on the conclusions of Ruer with regard to the action of simultaneous alternating and direct currents on platinum anodes is discussed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 25, June 18, 1906.

Researches on Direct Synthesis of Nitric Acid and Nitrates from their Elements at Ordinary Temperatures.—M. Berthelot.—The author makes a series of researches on the synthesis of nitric acid from its elements at ordinary temperatures under the influence of an electric current obtained from an induction coil with alternate discharges augmented by a 12-volt current of 6 ampères. The reaction seems to take place according to the exact equation $N_2 + O_3 + H_2O + Aq = 2NO_3H$ dilute.

Action of Carbonic Oxide on Water-vapour at a Red Heat and of Hydrogen on Carbonic Acid. Application of these Reactions to an Investigation of Volcanic Phenomena.—Armand Gautier.—When carbonic oxide acts on water-vapour at 1200—1250°, CO_2 , H_2 , CO , and atmospheric nitrogen result, the numbers showing the reaction (1) $3CO + 2H_2O = 2CO_2 + 2H_2 + CO$ to have taken place. This equation does not vary sensibly if the quantity of water introduced is varied. When hydrogen acts on carbonic acid at a high temperature the CO_2 is reduced, forming water, (2) $CO_2 + 3H_2 = CO + H_2O + 2H_2$, after which reaction (1) takes place.

Use of Metallic Oxides as Oxidising Catalysers.—Paul Sabatier and Alphonse Mailhe.—If vapour of formic carbide mixed with a current of oxygen is directed on to

oxide of copper, the temperature of the oxide being gradually raised at about 200°, an incandescence becomes apparent, which is maintained indefinitely as long as the current of mixed gases is used. The heating can gradually be stopped without interfering with the phenomenon. Oxidation is also produced with permanent incandescence if the copper oxide is replaced by nickel or cobalt oxide. The experiment succeeds with methane as well as with various liquid carbides, pentane, hexane, heptane, &c.

Reduction of Antimony Selenide.—P. Chrétien.—When Sb_4Se_3 is reduced by adding antimony, two temperatures of fusion are observed, but the two temperatures are of unequal and variable importance. An analysis of the mass shows that there are two solutions of very different concentration. The existence of these two phases is only due to a defective mixture. The author now makes a new series of measurements starting from $SbSe$, and adding an intimate mixture of finely powdered antimony and selenium. A single temperature of fusion is then noticed, but again starting from the same point and adding increasing proportions of antimony, the two phases appear as before.

Oxidations due to Air. Problem of the Comparison of Velocities.—André Job.—The author finds that oxidations by means of air are very difficult to define. Measurements, even when only relative and of simple comparison, are often illusory. They are only of value if very severe rules are imposed which require very delicate experimental technique. The author worked under the following conditions:—Very violent agitation of the liquid with air in an hermetically sealed apparatus, rigorously constant temperature, &c. By reason of the difficulties and even after numerous experiments he still could not obtain definite concordant results.

Heterogeneous Equilibria. Formation of Phosphonium Chloride, Carbamate, and Ammonium Sulphohydrate.—E. Briner.—The author gives an account of his experiments performed to verify theoretic considerations described in a previous paper (*Comptes Rendus* of May 28th, 1906); the systems ($CO_2 + 2NH_3$) and ($NH_3 + H_2S$) being investigated.

Osmotic Pressure in Hydrochloroferric Colloid.—G. Malfitano.—When a preparation of hydrochloroferric colloid obtained by heating a 0·5 per cent solution of Fe_2Cl_6 for fifteen minutes to 115—120° is filtered, a liquid residue remains. If after keeping the interior pressure constant until the volume reaches a limit, the apparatus is then put under ordinary pressure, leaving the filter in contact at its lower extremity with the liquid filtrate, the latter re-enters the filter and the level rises inside. The author measures the osmotic pressure of such a colloidal solution.

Copper Steels.—Pierre Breuil.—The author investigates the properties of copper steels, and finds that the copper considerably raises the hardness of the steel. He investigates two series with varying proportions of copper by means of the Le Chatelier thermoelectric couple.

Melezitose and Turanose.—Georges Tanret.—Turanose, $C_{12}H_{22}O_{11}$, is not, as was hitherto believed, able to be decomposed into two molecules of glucose. On hydrolysis it breaks up into one molecule of glucose and one molecule of levulose. Melezitose, $C_{18}H_{32}O_{16}$, gives, by feeble hydrolysis, a molecule of glucose and a molecule of turanose. It is formed of two molecules of glucose and one molecule of levulose.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Hydrochloric Gas Generating Vessel.—Can any reader kindly tell me the best firm to apply to for a small vessel generating about 40 lbs. of hydrochloric gas per day of eight hours. Also small centrifugal separator taking 10 lbs. of material in one operation.—H. J.

THE CHEMICAL NEWS.

VOL. XCIV., No. 2435.

ON THE ULTRA-VIOLET SPECTRUM OF YTTERBIA.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

THE rare earth ytterbia was discovered in 1878 by Marignac (*Comptes Rendus*, vol. lxxxvii., p. 578). In 1880 Nilson (*Ber.*, vol. xii., p. 554), in purifying Marignac's ytterbia, found that it contained another earth which he named scandia. Cleve, and more recently his daughter Astrid Cleve, have worked much on ytterbia, and within the last few years M. Urbain has taken up the subject, and has succeeded in purifying ytterbia in larger quantities. During my own work on the fractionation of the rare earths I also have prepared and worked with ytterbia.

Marignac, Nilson, Cleve, and Urbain have each presented me with some of their ytterbia. Nilson's earth, sent in 1886, appears pure. Unfortunately, there was only sufficient to enable me to photograph the part of its spectrum between wave-lengths 2400 and 2580.

Ytterbia is one of the least basic oxides of the yttria group; the order being yttria, erbia, thulia, ytterbia, and scandia; yttria being the most basic and scandia the least. The atomic weight of ytterbium, taking the formula of the oxide, the only one known, as Yb_2O_3 , is, according to Nilson, 173.01. Miss Astrid Cleve obtained the number 173.11. The salts of ytterbium are colourless and show no spectrum bands by transmitted light.

My ytterbia was prepared from the mixed yttria earths by the old method of partial decomposition of the nitrates by heat. The chief difficulty is to free the ytterbia from the last traces of thulia. The fractionation of the nitrates must go on until a considerable thickness of the fused nitrate shows no trace of the thulium absorption bands at wave-lengths 4700 and 7000. A trace of scandia may still be present, but this earth is very seldom met with. All my tests have failed to show its presence, and Miss Cleve, working with several kilograms. of ytterbium earths derived from different minerals, also was unable to find scandium in them.

In April, 1904, M. Urbain gave me sufficient of his purest ytterbia to enable me to photograph its complete ultra-violet spectrum. His earth was prepared by the fractional crystallisation of the ethyl-sulphates of crude gadolinite earths (*Comptes Rendus*, vol. cxxii., p. 136). The subsequent separation is by the fusing nitrate method. This after twenty series of fusions gave in the least basic portions a mixture of ytterbia and thoria, which are easily separated by Wyruboff and Verneuil's method. This is the ytterbia of which I have photographed the spectrum. It still contains traces of thulia. M. Urbain's more recent method of preparing ytterbia is by fractionally crystallising the nitrates from a slightly diluted nitric acid. In this way he tells me he has succeeded in getting ytterbia free from thulia.

The examination for absorption-bands in a strong solution is a fairly good test for an earth, such as erbia and thulia, giving absorption spectra, but it is not so delicate as an examination of the spark spectrum photographed through a quartz train, for dominant lines which most elements show in some part of their spectrum. For instance, the dominant lines of yttrium are at wave-lengths 3600.9, 3710.4, 3774.5, 4177.7, and 4375.1. The dominant lines of erbium are at 3499.3, 3692.8, and 3906.5. They are, however, not strong, and fortunately the absorption bands of this element are striking and characteristic. The spark spectrum of thulium has only been slightly examined

by me, and I do not think it has any strong lines. Its absorption spectrum, as with erbium, is a very characteristic one. The spark spectrum of ytterbium has strong dominant lines at 3289.5 and 3694.4. Scandium has dominant lines at 3572.7, 3614.0, 3630.9, 3642.9, and 4247.0.

The spark spectrum of ytterbium was first examined by Thalen, but only in the visible portion. Exner and Haschek have published a set of measurements of the spark spectrum of ytterbium, from wave-lengths 2116 to 4726 ("Wellenlängen-Tabellen für Spektralanalytische Untersuchungen," F. Deuticke, Leipzig und Wien, 1902). I have found them to be very accurate, and in my photographs I have generally adopted their figures. Occasionally lines are in their list which appear to belong to other elements, and in some cases lines given by them cannot be distinguished in my spectrum.

My photographs were taken with the quartz apparatus already described, the spectrum of pure iron being used as a standard. The ytterbium spark was taken from a strong solution of the nitrate between platinum poles, sufficient self-induction being introduced to eliminate nearly all the air lines. The ytterbium, by this very severe spectrum test, is seen to be not absolutely free from impurities, thulium,* copper, and calcium being present. Thulium is seen by its lines at 3020.7, 3131.4, 3425.2, 3441.6, 3462.4, and 3848.2. Copper is seen by its dominant lines at 3247.7 and 3274.1, and calcium by its dominant lines at 3933.8 and 3968.6.

The platinum lines which are present are easily recognised, and are useful as an additional measure of identification. Besides these a number of fainter and indistinct lines are seen. These may be due to ytterbium, or to traces of hitherto unrecognised impurities.

The wave-lengths of all the recognisable lines of ytterbium are given on the photograph, and also those of thulium, calcium, and copper, but the platinum lines are not marked.

NOTES OF A COURSE OF LECTURES ON THE OLD AND NEW CHEMISTRY.†

II. EXTRACTS FROM DIFFERENT AUTHORS RELATING TO THE NEW CHEMISTRY.

By Prof. Sir JAMES DEWAR, F.R.S., &c.

Continued from p. 26).

History of the Advent of the New Chemistry.— Thomas Young.

"CONTENTING ourselves with enumerating the names of Roger Bacon and Basil Valentine, as the greatest chemists of the thirteenth and fifteenth centuries, and Paracelsus, Agricola, and Libavius, of the sixteenth, we shall hasten to the beginning of the seventeenth, as the true period of the commencement of the pneumatic chemistry, under the auspices of Van Helmont, who first distinctly observed the properties of several elastic fluids, which he denominated gases; and more especially of Rey, who, in the year 1630, expressly maintained the absorption of air by metals during their calcination; nor was it much later that Torricelli and Pascal began to investigate the mechanical properties of the air with mathematical precision. About the time of the foundation of the Academy del Cimento, of the Royal Society, and the Parisian Academy of Sciences, which constitutes an era so important in the progress of human knowledge, the most distinguished chemists in

* M. Urbain writes, under date May 5th, 1906:—"The ytterbium of which you have taken the spectrum was prepared some years ago. It is impossible to affirm that it does not contain thulium, and the experience I have acquired since these already ancient researches leads me to think it does contain traces. Thulium is very difficult to separate completely from ytterbium, and I have only recently succeeded in doing so. Do not fail to mention that this preparation was obtained by fusion of the nitrates of the rose-coloured yttric earths obtained in the tails of the crystallisation of the ethyl sulphates."

† Delivered at the Royal Institution, May 26th, 1906.

* A Paper read before the Royal Society, June 28, 1906.

Germany were Glauber, Kunckel, Brandt, Hofmann, Beccher, and Stahl; in France, Homborg, Geoffroy, and the Lemerys; and in England, Boyle, Hooke, Slare, and Mayow; but with regard to the philosophical theory, especially of pneumatic chemistry, the English had advanced far beyond their neighbours, even before the publication of the correct and comprehensive speculations contained in the queries of Newton, which marked the commencement of the eighteenth century, and which may be considered as the basis of the more refined and accurate cultivation of chemical science. In pursuit of these suggestions, the order of chemical attractions appears to have been first distinctly exhibited in a tabular form by Geoffroy, about the year 1718. The idea of a single combustible principle, or phlogiston, is traced to Albertus Magnus, the contemporary of Roger Bacon, and was received from Beccher by Stahl, who advanced in support of it many ingenious experiments; for example, the decomposition of Glauber's salt by charcoal; and this doctrine was almost universally adopted throughout Europe in preference to the more correct views of Boyle, Hooke, and Mayow. The researches of these chemists were, however, in some degree revived by the industrious Dr. Hales, although he was unfortunately misled by the idea that all elastic fluids were essentially the same, and only distinguished by some accidental modifications from the presence of various effluvia. The error of this opinion was clearly and elegantly displayed by Dr. Black, who published, in 1756, a little essay on magnesia and fixed air, which may be considered as the true beginning of the pneumatic chemistry. The earliest labours of Mr. Cavendish are dated in 1765, when he invented the hydropneumatic apparatus, discovered inflammable air, and made very many important experiments on the properties of gases of different kinds. Dr. Priestley followed the steps of Hales and Cavendish with the most distinguished success, and discovered the existence of nitrous gas, nitrous oxyd, and oxygen; and exhibited by means of the mercurial apparatus, muriatic acid, sulphurous acid, and ammonia in a gaseous state. Macquer, Rouelle, Margraff, Pott, and, above all, Bergman, were in the meantime diligently pursuing their refined analyses on the Continent; and Scheele was carrying on a train of investigations much resembling those of Priestley, ascertaining the composition of the atmosphere, and the properties of the fluoric and prussic acids, and the oxy-muriatic acid gas. Of all these chemists, Black, Cavendish, Priestley, and Scheele were unquestionably the greatest discoverers; the facts which they had brought forward were in some measure systematised by Lavoisier, to whom our author thinks that 'no other inquirer except Cavendish can be compared for precision of logic, extent of view, and sagacity of induction.' Bayen, in 1774, had shown that the calx of mercury was capable of being rendered metallic without the addition of any inflammable substance, and hence had argued against the agency of phlogiston in the revival of metals in general. In the next year, Lavoisier examined the air afforded by the calx during its reduction, which was already known to Priestley and Scheele, and called it oxygen; he demonstrated also the constitution of the carbonic acid gas, and showed that the nitrous and sulphuric acids derive their properties from the combination of their bases with oxygen. Mr. Cavendish soon after showed the true nature of the basis of the nitric acid, and made a discovery, which is perhaps of greater importance than any single fact which human ingenuity has ascertained, either before or since, that of the composition of water from oxygen and hydrogen. Soon after this, Mr. Berthollet proved that ammonia consists of hydrogen and nitrogen, and many other chemists continued a series of researches, which appeared to illustrate and confirm the doctrine of Lavoisier. The existence of phlogiston was, however, still very ably maintained by Mr. Cavendish, in 1784 as the simpler of the two theories by which the phenomena might be explained; and other chemists retained the same opinion for a much longer period. In 1787, the French chemists presented to the public their

new system of nomenclature, which certainly contributed in some degree to the faculty of acquiring the science, but still more to the dissemination of the doctrines of the school from which it proceeded."

Cavendish.—Thomas Young.

"In 1760 he became a Fellow of the Royal Society, and continued for almost fifty years to contribute to the *Philosophical Transactions* some of the most interesting and important papers that have ever appeared in that collection, expressed in language which affords a model of concise simplicity and unaffected modesty, and exhibiting a precision of experimental demonstration commensurate to the judicious selection of the methods of research, and to the accuracy of the argumentative induction; and which have been considered, by some of the most enlightened historians, as having been no less instrumental in promoting the further progress of chemical discovery, by banishing the vague manner of observing and reasoning that had too long prevailed, than by immediately extending the bounds of human knowledge with respect to the very important facts which are first made public in these communications.

"The splendid career of chemical investigation, which has since been pursued with a degree of success so unprecedented in history, may be said to have been first laid open to mankind by the labours of Mr. Cavendish; although the further discoveries of Priestley, Scheele, and Lavoisier soon furnished, in rapid succession, a superstructure commensurate to the extent of the foundations so happily laid. 'Whatever the sciences revealed to Mr. Cavendish,' says Cuvier, 'appeared always to exhibit something of the sublime and the marvellous; he weighed the earth; he rendered the air navigable; he deprived water of the quality of an element'; and he denied to fire the character of a substance. 'The clearness of the evidence on which he established his discoveries, so new and so unexpected as they were, is still more astonishing than the facts themselves which he detected; and the works, in which he made them public, are so many masterpieces of sagacity and of methodical reasoning; each perfect as a whole, and in its part, and leaving nothing for any other hand to correct, but rising in splendour with each successive year that passes over them, and promising to carry down his name to a posterity far more remote than his rank and connections could ever have enabled him to attain without them.'"

Priestley.—Prof. Thomson.

"His discoveries in pneumatic chemistry are so numerous, that I must satisfy myself with a bare outline; to enumerate everything, would be to transcribe his three volumes, into which he digested his discoveries.

"The first of his discoveries was nitrous gas, now called deutoxide of azote, which had, indeed, been formed by Dr. Hales; but that philosopher had not attempted to investigate its properties. Dr. Priestley ascertained its properties with much sagacity, and almost immediately applied it to the analysis of air. It contributed very much to all subsequent investigations in pneumatic chemistry, and may be said to have led to our present knowledge of the constitution of the atmosphere.

"The next great discovery was oxygen gas, which was made by him on August 1, 1774, by heating the red oxide of mercury, and collecting the gaseous matter given out by it. He also immediately detected the remarkable property which this gas has of supporting combustion better, and animal life longer, than the same volume of common air; and likewise the property which it has of condensing into red fumes when mixed with nitrous gas. Lavoisier likewise laid claim to the discovery of oxygen gas; but his claim is entitled to no attention whatever, as Dr. Priestley informs us that he prepared this gas in M. Lavoisier's house, in Paris, and showed him the method of procuring it in the year 1774, which is a considerable time before the date assigned by Lavoisier for his pretended discovery. Scheele, however, actually obtained this gas without any

previous knowledge of what Priestley had done; but the book containing this discovery was not published till three years after Priestley's process had become known to the public.

"Dr. Priestley first made known sulphurous acid, fluosilicic acid, muriatic acid, and ammonia in the gaseous form; and pointed out easy methods of procuring them. He describes with exactness the most remarkable properties of each. He likewise pointed out the existence of carburetted hydrogen gas; though he made but few experiments to determine its nature. His discovery of protoxide of azote affords a beautiful example of the advantages resulting from his method of investigation, and the sagacity which enabled him to follow out any remarkable appearances which occurred. Carbonic oxide gas was discovered by him while in America, and it was brought forward by him as an incontrovertible refutation of the antiphlogistic theory.

"Though he was not strictly the discoverer of hydrogen gas, yet his experiments on it were highly interesting, and contributed essentially to the revolution which chemistry soon after underwent. Nothing, for example, could be more striking than the reduction of oxide of iron, and the disappearance of the hydrogen when the oxide is heated sufficiently in contact with hydrogen gas. Azotic gas was known before he began his career; but we are indebted to him for most of the properties of it yet known. To him, also, we owe the knowledge of the fact that an acid is formed when electric sparks are made to pass for some time through a given bulk of common air; a fact which led afterwards to Mr. Cavendish's great discovery of the composition of nitric acid.

"He first discovered the great increase of bulk which takes place when electric sparks are made to pass through ammoniacal gas—a fact which led Berthollet to the analysis of this gas. He merely repeated Priestley's experiment, determined the augmentation of bulk, and the nature of the gases evolved by the action of the electricity. His experiments on the amelioration of atmospherical air by the vegetation of plants, on the oxygen as given out by their leaves, and on the respiration of animals, are not less curious and interesting."

"Lavoisier."—Samuel Brown.

"It was Antoine Laurent Lavoisier who first felt the pressure of the necessity for a renovated theory of chemistry, and at once began to construct it, say rather to woo it from the opening bosom of nature, where it lay ready to come forth at the call of him who knew the word of power. Dumas has triumphantly shown that his countryman had formed the idea of his great revolution at the very outset of his career, and that even before many of the pneumatic discoveries of the Swedish and British phlogistians had been made and published. There can be no manner of doubt, in fact, of the single-handed originality of the French law-giver of chemistry in bringing about that transition, from the era of phlogiston and the cupel to that of oxygen and the balance, which constitutes the turning-point of the history now under review. It is easy and social to speak with effusion about the division of labour and the grandeur of combination; but it seemed generally to be individual men that do the greater business of science and of the world after all. Institutes, academies, royal societies have all been good; but a man like Lavoisier is better than them all. German, British, American associations have their important purposes to serve, and they subserve them well; but an opinion begins to prevail, that in these days we run some danger of being associated to death. Excessive association certainly tends to the production of weakness in the individual unit, if the resulting whole is strong; and it is fortunate that there are some men so unsocial as to dwell apart, drawing inspiration from the quiet past, from the instant universe itself, and from the whispering dawn that is ever arising in the East.

"The Lavoisierian definition of the elemental nature was perfect. It was the first clear conception ever attained to

and uttered on the subject. This great law-giver of chemistry became positive, an apt scholar in scientific scepticism, and the admirer of Condillac, defined a chemical element to be nothing more, and nothing less, than a material substance not yet analysable, not yet broken up into simpler forms; in short, a body not yet decomposed, but not, therefore, indecomposable to be called simple for the time being, but not necessarily always to remain in the list of elements; elementary not in an absolute but only in a logical and provisional sense of the term. The metals, the earths, the alkalis, the combustibles, the three gaseous organogens were therefore all registered as elements for the meantime. Davy decomposed the alkalis and earths, proving them to be the oxides of so many new and unheard-of metals. The same chemist, certainly the noblest of the disciples and workmen of Lavoisier, found out the true nature of chlorine, and thereby deprived oxygen of the right to its name; for oxygen had been prematurely chronicled as the acid-generating element, but chlorine was now discovered to be at once a simple body and an engenderer of acids just as truly as oxygen.

"Iodine, selenium, silicon, titanium, rhodium, and many other substances, equally elementary with oxygen and the old metals, have followed in their turns, and there are now no fewer than some sixty Lavoisierian elements, while there may well be a hundred of them before the century is out. There is no probable limit in truth to the number of this species of elementary principle. If the chemist could but dig deeper into the surface of the world he inhabits, or could be licensed to carry his quarrying gear to the moon, or could even lay hold of the smallest of the Junonian asteroids, to say nothing that might be construed into impertinence concerning the diggings of either Jupiter or Venus, what a pile of such simple bodies he might build up! It should never be forgotten that he has hitherto done nothing but scratch the outside of this old Hertha, and that only to the depth of the thickness of this paper leaf in comparison with a sphere of 2 feet in diameter. In fact and in brief then, there may be six hundred of such elements as ours, just as well as sixty; and almost every year is actually adding a new one to the catalogue. In the meantime, it is to be understood that, from not one of these present sixty, can the hottest furnace, seven times heated, the coldest freezing mixture, the strongest and steadiest galvanic pile, the most thunderous of electric batteries, or the most pungent reagent, were it even fluorine or potassium at a white heat, extract anything but itself. Gold yields gold, iron yields iron, hydrogen yields hydrogen, only gold and iron and hydrogen, to all the solicitations of the fiercest analytics yet known. We stand before the guarded door of nature; the strong bolts will not move; everything fails us, everything!

"Yet it is hard to think that all those sixty creatures are truly simple or elementary. The instinct of humanity revolts against believing that the Maker has departed from His wonted simplicity of procedure in this one part of creation, and flung such a number of unchangeable elements from His immediate hand. Many thoughtful and ingenuous men, indeed, have frankly supposed that it were more like the nature of the Deity, as shown by his interpreted works, to pour forth the unreckonable variety of things from the bosom of one or two principles. Thales and the Greek physicists, Geber and the polypharmists, Roger Bacon and the alchemists, Stahl and the phlogistians, Lavoisier himself, Humphry Davy, Prout, even Berzelius, that man of multitude, have all given more or less explicit expression to this native yearning of the thoughts of the heart of man towards simplicity; that is to say, towards some unity or other underlying the multiplicity of appearances, in this subterranean domain of nature. Man does not love multiplicity, he admires it; but it is unity that he loves, for it moves his imagination while it touches his heart, not only making the whole world kin, but also lessening the distance between that world and God. The next great question in chemistry, then, say rather the per-

petual, and the greatest question in the science, is precisely this:—What is the interior nature of those elements? From the Lavoisierian point of view, in plain earnest, that is the one question of the age. The science bids us ask, and perhaps nature is ready to answer it; but what shall be done, since no known analytical power can move one of those steadfast natures from its propriety? Let synthesis be tried, if analysis has failed; synthesis has never been tried. Be it observed, too, that it is in the highest degree probable that all the sixty present elements are equidistant from simplicity; they are all equally compound (and equally simple, for that matter), if there be any truth in the unanimous testimony of chemical analogy."

Berzelius, Mitscherlich, Herschel, and Liebig, on the Atomic Theory of Dalton.

Berzelius, in 1835, said, "The atomic hypothesis was afterwards confirmed by numerous experiments, and we may state without exaggeration that this is one of the greatest steps which chemistry has yet made towards perfection." Mitscherlich, about the same date, said, "that this hypothesis, like every other, must undergo changes in proportion as observations are multiplied. It is possible, although highly improbable, that it may be wholly superseded by another; yet the history of science can adduce scarcely any law, and certainly no theory, which has conducted the inquirer to so many discoveries as this hypothesis; it has served as a guide, not merely in the discovery of the law of definite proportions, but also in many investigations which have given the most important results."

Sir John Herschel, in 1831, said, "The atomic theory, or the law of definite proportions, which is the same thing presented in a form divested of all hypothesis, after the laws of mechanics is, perhaps the most important which the study of nature has yet disclosed. The extreme simplicity which characterises it, and which is itself an indication, not unequivocal, of its elevated rank in the scale of physical truths, had the effect of causing it to be announced at once, by Mr. Dalton, in its most general terms, on the contemplation of a few instances, without passing through subordinate stages of painful inductive ascent by the intermedium of subordinate laws, such as, had the contrary course been pursued by him, would have been naturally preparatory to it, and such as would have led others to it by the prosecution of Wenzel's and Richter's researches, had they been duly attended to."

Liebig, in 1853, said, "Dalton's atomic theory was a product of the age, and sprang forth in his mind, as a consequence of the discovery of chemical proportions or equivalents. By means of this theory, the numerical results were connected with definite representations concerning the internal nature and constitution of chemical combinations; and thus a number of researches were called forth and prepared for, which had for their object the relations of physical properties to internal composition. I need refer only to isomorphism, to the relations of the specific heat, to the atomic weight, and to those of the boiling-point to composition. Chemistry received in the atomic theory, a fundamental view, which overruled and governed all other theoretical views, to which the ideas of the age respecting chemical forces, affinity, cohesion referred themselves; it was the bond which bound together all other views. In this lies the extraordinary service which this theory rendered to science, viz., that it supplied a fertile soil for further advancement; a soil which was previously wanting. In the most recent investigations concerning the constitution of organic bases, the alcohols and the acids corresponding to the alcohols, we have seen that the groundwork of the Daltonian theory is equally valid for organic bodies. His main law that the properties of compounds are dependent on the nature of their elements, and on the mode and way of their position or arrangement, will always maintain a high value."

(To be continued).

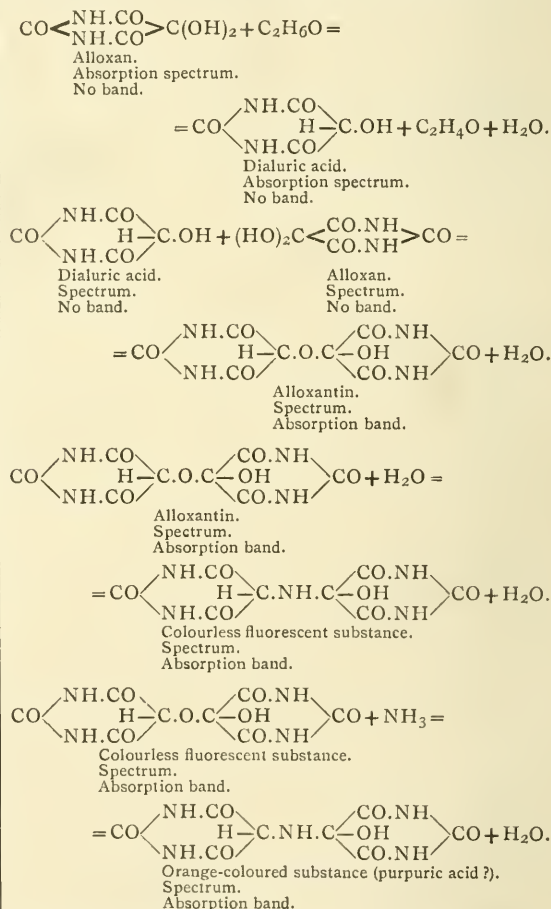
THE STUDY OF ABSORPTION SPECTRA IN RELATION TO THE CHEMICAL STRUCTURE OF COLOURLESS AND COLOURED SUBSTANCES.*

By WALTER NOEL HARTLEY, F.R.S.,
Royal College of Science, Dublin.

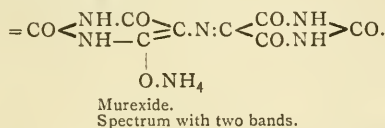
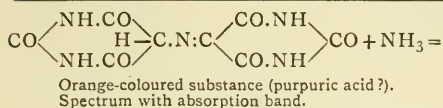
(Concluded from p. 31).

A SUBSTANCE which shows a spectrum with an absorption band in the ultra-violet is a chromogen, and by suitable reactions it may be made to assume colour. The application of this knowledge is of interest to the colour chemist, and therefore a sketch of the results of an investigation recently published (*Chem. Soc. Trans.*, 1905, lxxxvii., pp. 1791—1831) may, I trust, prove an acceptable contribution to this section as explaining the evolution of colour from such colourless materials as the ureides.

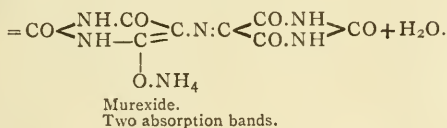
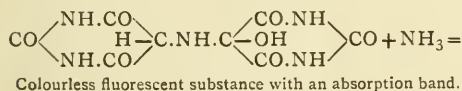
Murexide may be prepared by boiling alloxan, and also alloxantin with absolute alcohol saturated with ammonia gas. The steps in the process are as follows:—One molecule of alloxan is first reduced to dialuric acid by a molecule of alcohol; it then unites with a molecule of alloxan to form alloxantin, water being eliminated. The action of ammonia on the alloxantin causes the formation of a colourless fluorescent, unstable substance, and a scarlet or orange-coloured compound, apparently a purpuric acid. The purpuric acid with aqueous ammonia yields murexide. The following equations will explain this action:—



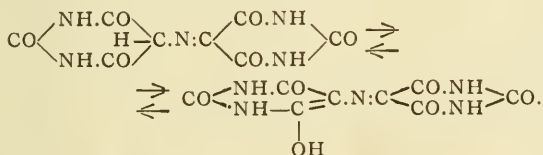
* A Paper read at the Sixth International Congress of Applied Chemistry, Rome, April 27th, 1906.



The action of the second molecule of ammonia in the boiling solution may receive another interpretation, thus:—



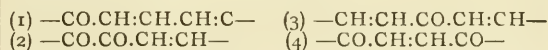
It is probable that two isomerides are formed in the reaction, both of the nature of purpuric acid, one of which combines with ammonia (NH₃) in alcoholic solution, and the other with ammonium hydroxide only; that is to say, in aqueous solution. The latter corresponds with the orange-coloured substance which has been isolated. The evidence of this is a reaction described by Max Stimmer and Stieglitz, who converted alloxantin entirely into murexide by heating with alcoholic ammonia in sealed tubes for twenty-four hours (Max Stimmer and Stieglitz, *Amer. Chem. Jour.*, 1904, xxxvii., 2686).



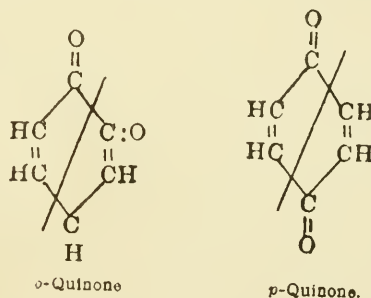
The essential conditions for the formation of a colour, such as murexide, are, first, the linking of two oximino-ketone rings by oxygen or by nitrogen; secondly, the formation of one or more ethylenic linkings within in one of the rings; and thirdly, the formation of a salt from this compound.

The recent discovery of carbon sub-oxide by Otto Diels and Bertram Wolf (*Ber.*, 1906, xxxix., 689), with the description of its remarkable properties, appears to me of the highest importance in connection with investigations into the relationship between chemical structure and the colour of organic compounds. This substance, obtained from ethyl malonate by the dehydrating action of phosphoric anhydride, is a colourless gas which may be condensed to a volatile liquid boiling at 7°. From its mode of preparation, its reactions, and its vapour density, the authors have assigned to it the formula, —OC:C:CO—. Its most remarkable property is that of spontaneously changing at ordinary temperatures into a coloured substance. The liquid when contained in a sealed tube first turns a feeble yellow colour, then yellow flocks separate, which become darker, and finally acquiring a dark red colour, the contents of the tube become solid. The solid substance when powdered appears almost black, but it readily dissolves in cold water, forming an extraordinarily intense eosine-red solution. What the precise nature of the change is cannot be positively affirmed, but there can be little doubt about its being polymerisation. Certain un-

saturated ketones have been recognised as containing the following chromophoric groups:—

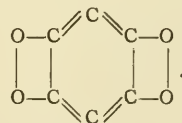


(Haller and Kostanecki, also Kostanecki and Rossbach, *Ber.*, 1897, xxx., 2947), and it was shown by Wallach (*Chem. Centralblatt*, 1897, i., 373), that the introduction of an ethylenic linking adjacent to a carbonyl group produces a greater absorptive power for the violet rays in a derivative than that possessed by the parent substance, and hence when the latter is colourless the derivative is green or yellow. It is important to note that the substance need not be derived from an aromatic nucleus, since Wallach's observations were made on open chain ketones, and also, if the carbon atoms on both sides of the C:O group are attached to the rest of the molecule by ethylenic linkings, a still stronger colour is exhibited by the compound. Now in any ring structure this may more easily occur than in an open chain compound, and it has been pointed out that *o*-quinones have the same atomic groupings as the chromophores (1) and (2), and the *p*-quinones that of (3) and (4). Moreover, the chromophore —CH.C:O.CH:C— of the unsaturated ketone C₆H₅.CH:CH.C:(O).C₆H₅, or benzylideneacetophenone, not only occurs twice in the ring structure of the *o*- and *p*-quinones, but in fact both substances are entirely composed of this chromophore, as may be seen by dividing their structural formulæ by a diagonal line.



The importance of the ethylenic linking in conjunction with the carbonyl group is also exemplified in murexide, in which the double linking of the atoms results from the condensation of two ureides into one diureide.

The carbon suboxide is manifestly a chromogen —O.C:C:O— and if one may be allowed to deduce a constitutional formula for the red substance into which it spontaneously changes, there is reason to believe on the evidence of the foregoing facts that it is a cyclic compound with the following structure:—



As it contains no hydrogen, it is a most interesting substance in its relations to colour and chemical structure.

Refractive Index of Bodies Dissolved in Solvents other than Water.—C. Chéneveau.—The author makes a series of determinations of refractive indices and densities of solutions containing one salt and one liquid other than water. His experiments were made with one of the salts LiCl, CaCl₂, CuCl₂, SnCl₂, MgCl₂, dissolved in ethylic alcohol, LiCl in methylic alcohol, ZnCl₂ in ethylic ether, and NH₄Cl in glycerin.—*Comptes Rendus*, cxlii., No. 26.

THE COAL-TAR COLOUR JUBILEE.

THE Theatre of the Royal Institution on Thursday morning presented an appearance which fully justified the decision of the meeting held at the Mansion House in February last, to pay all possible honour to Sir William Perkin, the father of the coal-tar colour industry, now that fifty years have elapsed since his memorable discovery. The place was as full as though the audience had gathered for a fashionable Friday evening, and the first few rows of benches were filled with delegates from nearly every part of the civilised world, gathered together to present their respects, their congratulations, their medals, and their addresses to the veteran hero of the great scientific festival. Happily for the effect of the gathering the somewhat funereal phalanx of black coats in the front was cheerfully framed by variegated colour, for ladies (of whom few can have attended the birth of the great discovery by virtue of which their costumes had been brightened), had assembled in large numbers to grace the occasion, which might otherwise have been all but too impressive in its solemnity. It seems to have occurred to only a few of them to robe themselves in the colour specially appropriate to the day, but the gentlemen who played leading parts in the performance were decorated with rosettes of mauve ribbon, and Professor Meldola, the Master of the Ceremonies, had conscientiously embellished his shirt-front with a mauve tie.

Sir William Perkin himself was conducted at eleven o'clock punctually, when the theatre was already thronged, to the chair of honour in front of the table, while Professor Meldola conducted the proceedings from the usual station of the lecturer. And then, when the roar of applause with which Sir William Perkin's entry was greeted had gradually died away, the proceedings began, and for two solid hours the gallant knight received volleys of glowing compliment in the name of all the scientific societies of Europe and America which had been able in any way to associate themselves with the appreciation of his great achievement. The addresses were so numerous that it is impossible in this brief record of the proceedings to enumerate them in detail. Professor Meldola, of course, began by presenting Sir William with the portrait painted, according to the decision of the February meeting, by Mr. Cope, A.R.A., the work in question hanging up on the screen behind. Beneath it, on a pedestal, was exhibited a replica of the marble bust of Sir William, to be set up in the rooms of the Chemical Society. Professor Emil Fischer, of the Deutsche Chemische Gesellschaft, followed on immediately with a tribute, in German, to the world-wide importance of Sir William's work, presenting him, in the name of the society he represented, with the Hofmann Medal. Those of the audience who understood the language were prompt to applaud its points, and perhaps in some cases the applause was echoed by those who did not understand. But before the meeting was over the many German speeches delivered had so familiarised the audience with the sound of the words "*herzliche Glückwünsche*" that these, at all events, could readily be picked out by the hearers.

Sir William himself spoke at some length in reply, both to Prof. Fischer and Prof. Haller, who presented him—on behalf of *La Société Chimique de Paris*—with the Lavoisier Medal. To Hofmann both he and others referred in terms of enthusiastic admiration, whilst Sir William himself contrived to variegate the somewhat monotonous, however gratifying, flavour of the proceedings with little anecdotes of his early scientific recollections. As the morning wore away, it became gradually impossible for him to do more than express in a few words the thanks that were due to the addresses that came pouring in from all sides, until the table with which he had been provided for the storage of his trophies was piled with rolls of paper, bound books, and documents representing degrees of foreign universities conferred upon him on this auspicious occasion. Not the least important of the paper

rolls was handed to Sir William by Lord Kelvin on behalf of the Royal Society.

The address of the Chemical Society was delivered by Professor Meldola himself, its President, who described how Sir William was one of the oldest members of that Society, having joined soon after the date of his famous discovery. For seventeen years he had been its Secretary, and for two its President. And, again, pleasant recollections of the past were evoked by Dr. Divers (who offered congratulations on behalf of the Society of Chemical Industry), he himself, as it happened, having been a school-fellow of Sir William's and his companion at the earliest stage of their chemical studies. At last the proceedings were brought to a conclusion by a comprehensive speech from Sir William himself, who moved from his previous position to the lecturer's place behind the table, and told stories of his first familiarity with that historic theatre in which he heard Faraday's lectures when he was a boy of fourteen. How little at the time could he have foreseen that only a few years later he would lecture there himself on a discovery of his own destined to prove of world-wide importance; how still less could he have dreamt that fifty years later he would be the honoured centre of that brilliant gathering. With graceful taste he reminded his audience that to others besides himself the success of his work was due; above all to his father, who had provided the means with which he established the factory where aniline dyes were originally produced. He dwelt on the satisfaction he felt in thinking that his work had contributed to provide employment for a vast army of working people, and thus had contributed to confer those benefits on mankind that constituted the highest rewards of scientific achievement. Incidentally he explained that in the beginning the silk dyers of France took very cordially to the new mauve dye, while at first the firms in this country connected with cotton dyeing held aloof. Then, by degrees, the French calico-printers realised the importance of the new discovery and began to adopt it freely, followed by our own more lethargic countrymen. As Professor Green, the Secretary of the Jubilee, pointed out, the Royal Institution was not merely a place appropriate to the celebration in progress, in all the world no place more fitting could have been found.

And thus the demonstration, saved by its genuine cordiality of feeling from growing tedious, came to a happy conclusion as regards its initial phase.

In the evening, a Dinner at the Whitehall Rooms closed the day's proceedings in a highly agreeable fashion. The Chair, of course, was taken by Professor Meldola, who had the guest of the evening on his right and on his left H.S.H. Prince Wilhelm zu Stolberg-Wernigrode, representing the German Embassy. Lord Halsbury gave a pleasant tone to the oratory in proposing "The Rulers of Foreign Nations," whom he humorously congratulated on minding their own business for the most part in the present age of the world. Mr. Haldane, the Secretary of State for War, proposed "The Health of Sir William Perkin," dwelling on the cosmopolitan aspect of science, which operated to render the present international gathering a demonstration in honour of a great individuality belonging to the world of Science as a whole. For want of talents for organisation on our part, it might be that the coal-tar colour industry had flitted across the North Sea, but he took credit for the practical genius of the English people, which enabled them, though they "muddled" matters in the beginning, to "muddle through" at all events in the end.

Sir William Perkin's reply dealt at some length with his earlier work, when it was not thought well for men of science to be concerned with practical industry. He defended the principle that original research should be the inspiration of manufacture.

About 170 guests enjoyed the admirably appointed banquet and the unusual intellectual value of the speeches which followed.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, July 5th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Reginald de Vere Cornwall, Medical and Public Health Dept., Salisbury, Rhodesia, S. Africa; Henry Ernest Crocker, 452, Slade Road, Gravelly Hill, Birmingham; James Herbert Dinwoodie, Johannesburg; Gopal Chandana Sen, M.A., 23, Bond Street, Leeds.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Shelton Gottlieb Agar; Robert Anderson; Percy Corlett Austin, M.A.; Arthur John Berry; William John Bowis, Ph.D.; Harold Calam, B.Sc.; John Denton; Lionel John Drinkwater; Bertie James Eaton; Bernhard Flürscheim, Ph.D.; Reginald William Malyon Gibbs, B.Sc.; Thomas William D. Gregory; Edgar Percy Hedley; Charles H. Hertz, Ph.D., Ph.B.; Arthur Edwin Hill; Frederick Gowland Hopkins, M.A., M.B., D.Sc., F.R.S.; John Gerard Hughes; Ernest Arthur Jenkinson; Thomas Macdonald; Frederick James Martin; Herbert Arthur Mills; William Rest Mummery; Arthur Charles Palmer, B.Sc.; Leonard Edward Beard-Pearse; Harold Lawson Pendlebury; Percy George Pennymore; Samuel Shrowder Pickles, B.Sc.; Thomas Ebenezer Pye; Walter Hansen Rawles; Frederick John Salmon; Surendra Prasad Sanyal, D.Sc.; Willie Macro Seaber, B.Sc.; John Senior; Arthur Burton Shepherd, B.Sc.; Allan Sime; Fred Smith; Emanuel George Streimer; Richard Lumley Treble, B.Sc.; Robert Hutchison Turnbull; James Neil Watts; Charles Wightman; Edward Jocelyn Wortley; Henry Wren; George Young, B.A., B.Sc.

Of the following papers, those marked * were read:—

*132. "Saponarin; a New Glucoside Coloured Blue with Iodine." By GEORGE BARGER.

Dissolved in the cell sap of the leaf epidermis of various plants, there occurs a substance which is coloured blue by iodine, and which is known to botanists as "soluble starch." This substance has been isolated from *Saponaria officinalis*, and is a glucoside; the name saponarin is suggested for it.

Saponarin crystallises in microscopic needles melting at 231—232°, and having the composition $C_{21}H_{24}O_{12} \cdot 2H_2O$. The glucoside dissolves in alkalis with a yellow colour, gives with ferric chloride a reddish brown coloration, and with iodine a substance closely resembling that formed from starch.

Ennea-acetyl saponarin, $C_{21}H_{15}O_{12}(C_2H_3O)_9$, melts at 183—185° and crystallises in needles.

Acids hydrolyse saponarin, thus:—



yielding glucose and vitexin, a colouring matter obtained by A. G. Perkin from a New Zealand dye wood (*Trans.*, 1898, lxxiii., 1030, and 1900, lxxvii., 416).

At the same time another colouring matter is formed, apparently isomeric with vitexin, or closely related to it, for which the name saponaretin is suggested. Vitexin and saponaretin both yield phloroglucinol and *p*-hydroxy-acetophenone on boiling with caustic potash. Molecular weight determinations of vitexin and of acetyl vitexin prove that Perkin's formula, $C_{21}H_{20}O_{10}$, must be changed to $C_{17}H_{14}O_7$. Vitexin differs therefore from apigenin by two molecules of water, and probably is a flavanone derivative containing either a reduced pyrone ring or a reduced phloroglucinol nucleus. It would be a representative of a new class of colouring matters to which scoparin, which Perkin regards as methoxy-vitexin, would also belong.

DISCUSSION.

The PRESIDENT asked whether the new glucoside was

widely distributed in the vegetable kingdom, and whether it was contained in any considerable quantity in any particular plant. He also asked whether the isomeride of vitexin was, in the author's opinion, to be regarded as a natural product, or whether it resulted from the isomerisation of vitexin during the hydrolysis of the glucoside. He considered that Dr. Barger had satisfactorily established the identity of the product of hydrolysis of his glucoside with vitexin, and that he had also established the formula of the latter compound. He considered that the author had made an important contribution to plant chemistry.

Mr. GRANT HOOPER said that in the microscopic examination of vegetable substance, traces of what had hitherto been regarded as soluble starch were not infrequently observed. He would like to know whether Dr. Barger had detected and identified the interesting glucoside which he had just shown them in substances other than those from which he had isolated the new compound.

Dr. BARGER, in reply, said that saponarin, which is optically active, occurs in about twenty plants; one of the richest of these, namely, *Saponaria*, contains less than 1 per cent of the weight of dry leaves. Saponaretin is a product of secondary decomposition; vitexin is formed from the pure glucoside.

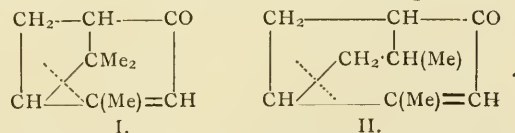
*133. "The Constitution of Umbellulone." By FRANK TUTIN.

The ketone, umbellulone, was isolated from the essential oil of *Umbellularia Californica* by Power and Lees (*Trans.*, 1904, lxxxv., 629), who showed it to possess the formula $C_{10}H_{14}O$.

The behaviour of umbellulone towards certain reagents was further studied by Lees (*Trans.*, 1904, lxxxv., 639), and its investigation has been continued by the present author.

Umbellulone, on oxidation, yields a saturated keto-acid, $C_9H_{14}O_3$ (m. p. 102°), called umbellulonic acid, which, on distillation under suitable conditions, is partially converted into an unsaturated lactone, $C_9H_{12}O_2$ (b. p. 217—220°). This lactone, on hydrolysis, yields umbellulonic acid, and is produced by the elimination of water from the enolic modification of the keto-acid. On oxidation, a polymethylene dicarboxylic acid, umbellularic acid, $C_8H_{12}O_4$ (m. p. 120—121°), is obtained, which is remarkably stable.

By the bromination of umbellulone, and subsequent distillation of the products, *p*-cymene was obtained, together with substances containing bromine. It would therefore appear that the molecule of umbellulone has a structure capable of yielding this hydrocarbon without undergoing any profound change. The only formulæ which offer a satisfactory explanation of the behaviour of umbellulone on oxidation and on bromination are the following:—



Both these substances, through the rupture of the bridge by the addition of hydrogen at the point indicated by the dotted line, would give compounds capable of yielding *p*-cymene. Formula I. represents a keto-pinene, which would yield, on oxidation, a dimethyltetramethylene dicarboxylic acid, identical or stereoisomeric with the norpic acid obtained by the oxidation of pinene. On the other hand, the compound represented by Formula II. would yield 1-methylpentamethylene 3:5-dicarboxylic acid.

It is considered most probable that Formula II. represents the constitution of umbellulone.

DISCUSSION.

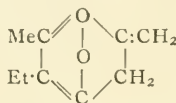
Dr. POWER congratulated Mr. Tutin on the accomplishment of this excellent work. He thought the evidence brought forward was so complete as to leave no doubt respecting the correctness of the constitutional formula

assigned to umbellulone by Mr. Tutin. It was of interest to note that only one other ketone possessing the same empirical formula as umbellulone, namely, carvone, had been observed to occur in nature, but this had a very different constitution.

*134. "The Action of Ethyl Iodide and of Propyl Iodide on the Disodium Derivative of Diacetylacetone." By ALEXANDER WILLIAM BAIN.

As the result of the action of ethyl iodide on the disodium derivative of diacetylacetone, suspended in alcohol, the following substances have been obtained:—

1. Dimethyldiethylpyrone, $C_{11}H_{16}O_2$ (m. p. 64°).
 2. Dimethylethylpyrone, $C_9H_{12}O_2$ (m. p. 58°).
- Each forms a hydrochloride and a platinichloride.
3. Diethyldiacetylacetone, $C_{11}H_{18}O_3$.
 4. A compound, $C_9H_{12}O_2$ (m. p. $66-67^\circ$, b. p. 289°), isomeric with dimethylethylpyrone, to which the formula—



ascribed. This compound on boiling with concentrated hydrochloric acid yields dimethylethylpyrone hydrochloride, and by the action of sodium hydroxide solution is changed into an orcinol derivative.

By the action of propyl iodide on the disodium derivative of diacetylacetone, the author has obtained dimethylpropylpyrone, $C_{10}H_{14}O_2$, and also an isomeric substance which possesses similar properties to the corresponding ethyl compound.

135. "A Possible Source of Error in Stas's Nitrogen Ratios." By ROBERT WHYTLAW GRAY.

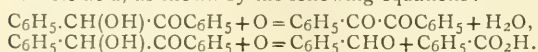
Stas's higher value for the atomic weight of nitrogen is supported by very little evidence.

Not only do the researches of Rayleigh, Leduc, D. Berthelot, Guye, and the author confirm the lower value, but an indirect comparison of the atomic weights of nitrogen and silver from the results of Marignac, Scott, and Richards leads to the same result.

By assuming similar errors in the ratio $\text{Ag} : \text{NH}_4\text{Cl}$ and $\text{Ag} : \text{NH}_4\text{Br}$ of Stas as those found for the ratio $\text{Ag} : \text{NaCl}$ by Richards and Wells, the value for nitrogen deduced is 14.011. The possible sources of error in the other ratios are discussed.

136. "Electrolytic Oxidation." By HERBERT DRAKE LAW.

On oxidising benzoin by the electrolytic method, three products are formed, namely, benzil, benzaldehyde, and benzoic acid, as shown by the following equations:—

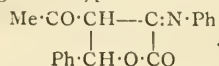


In addition to these, however, a certain amount of tarry matter is always obtained. This formation of complex tarry matter is a property of high potential discharge at the anode, and always takes place in the case of unsaturated compounds. The amount of any of these products which is formed is influenced very largely by the conditions of the experiment. Thus, strongly acid solutions promote the formation of tar, but none is observed when the anodic discharge is kept low. Similar experiments conducted with compounds resembling benzoin gave results agreeing with the above. Thus, cuminoil on being oxidised electrolytically forms cumic acid, cuminol, and tar. Furoin forms furil and tar, benzofuroin gives benzoic acid and tar, whilst anisoil and piperonyloin yield nothing but complex resinous matter of unknown constitution.

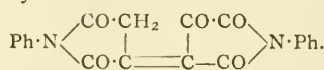
137. "The Ethyl Esters of Acetonyloxalic and Acetophenyloxalic Acids and the Action of Ethyl Oxalate on Acetanilide and its Homologues." By SIEGFRIED RUHEMANN.

The research was suggested by a note of Claisen's (*Ber.*, 1891, xxiv., 128) that ethyl sodioacetonyloxalate, on

boiling with glacial acetic acid, yielded the sodium compound possessing the empirical formula $\text{C}_5\text{H}_3\text{O}_3\text{Na}$. This is violet, as is the substance which Ruhemann and Merriman (*Trans.*, 1905, lxxvii., 1383) obtained in the course of their investigation on the reaction between phenylpropylol chloride and sodioacetylacetone. The compounds which are produced by the condensation of aromatic aldehydes with the ethyl esters of acetonyloxalic and acetophenyloxalic acids react with aniline and its homologues to yield yellow substances, which are constituted according to the type:—



With the object of ascertaining whether a relationship exists between these yellow substances and xanthoxalanil, which W. Wislicenus and Sattler (*Ber.*, 1891, xxiv., 1245) obtained, although in an impure form, from acetanilide and ethyl oxalate, the author has repeated the experiments of these chemists, and has prepared xanthoxalanil in a pure state by crystallisation from nitrobenzene; its constitution is expressed by the formula—



Similar compounds have been prepared by using, instead of acetanilide, aceto-*p*-toluidide (see Wislicenus and Sattler, *loc. cit.*), aceto-*o*-toluidide, and aceto-*a*-naphthalide. These substances differ from each other, especially in colour and solubility. Xanthoxalanil in deep orange and sparingly soluble in nitrobenzene xanthoxalo-*p*-toluidide, $\text{C}_{22}\text{H}_{16}\text{O}_5\text{N}_2$, is lighter in shade and more soluble, whilst the corresponding ortho-compound is canary-yellow and readily dissolves in this solvent; finally, xanthoxalo-*a*-naphthylanil, $\text{C}_{28}\text{H}_{16}\text{O}_5\text{N}_2$, is also yellow, but dissolves in glacial acetic acid.

138. "An Oxidation Product of Indigotin." By ARTHUR GEORGE PERKIN.

It has been shown by Sommaruga (*Annalen*, 1879, cxcv., 305) that, on sublimation under reduced pressure, refined natural indigo yields pure indigotin; again, Bloxam (*Trans.*, 1905, lxxvii., 982) has found that this is the case with the commercial synthetical product. With limited access of air, however, pure indigotin and also these commercial varieties give a small quantity of a yellow sublimate which crystallises in needles, m. p. $258-259^\circ$, is very sparingly soluble in alcohol, and can be distilled without appreciable loss. It appears to have the formula $\text{C}_{15}\text{H}_8\text{O}_2\text{N}_2$ (found, $\text{C}=72.59$; $\text{H}=3.17$; $\text{N}=11.59$ per cent), is very resistant to acid oxidising agents, but on boiling with strong potassium hydrate solution gives anthranilic acid. When treated in boiling glacial acetic acid solution with hydriodic acid, an unstable *hydriodide*, forming colourless, prismatic needles (found, $\text{N}=7.42$ per cent) is produced; this, on treatment with water, splits off hydriodic acid, and is re-converted into the substance $\text{C}_{15}\text{H}_8\text{O}_2\text{N}_2$; it is therefore probably the salt of an unstable reduction product of the latter. On reduction with tin and hydrochloric acid, a compound, $\text{C}_{15}\text{H}_{12}\text{ON}_2$ (found, $\text{C}=76.33$; $\text{H}=5.34$; $\text{N}=11.88$ per cent), crystallising in colourless needles, m. p. $190-193^\circ$, is formed, which on oxidation is re-converted into the substance $\text{C}_{15}\text{H}_8\text{O}_2\text{N}_2$. A trace of indole is also formed during the reduction. By the prolonged action of hydriodic acid, a compound crystallising in yellow needles, m. p. $200-203^\circ$, is produced, which can also be re-oxidised to the original product. The author hopes to devise a better method for preparing this yellow compound, as hitherto, with much labour, only 8 grms. of the pure substance could be obtained from 2 lbs. of indigo.

139. "Indigo-yellow." By ARTHUR GEORGE PERKIN.

In a previous communication (*Proc.*, 1904, xx., 172) it was shown that the yellow colouring matter usually present

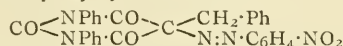
in Java indigo is kampherol. Examination has now shown that it is derived from a glucoside present in the leaves of the Java and Natal indigo plants (*Indigofera arrecta*), which is probably hydrolysed during the fermentation process. The material employed was chiefly the air-dried Natal leaf. This glucoside, for which the name *Kampheritrin* is proposed, has the formula $C_{27}H_{30}O_{14}$ (found, after being dried at 100° , $C=56.00$; $H=5.27$ per cent); the air-dried substance contains $3\frac{1}{2}$ mols. of water (found, $H_2O=9.79$ per cent). It crystallises in colourless needles, which are sparingly soluble in water, is very nearly devoid of tinctorial properties, and, when heated, congeals together at $190-192^{\circ}$, and melts at $201-203^{\circ}$. It is hydrolysed by acids according to the equation $C_{27}H_{30}O_{14} + 4H_2O = C_{15}H_{10}O_6 + 2C_6H_{14}O_6$ into kampherol (found, $C_{15}H_{10}O_6 = 49.19$ per cent) and rhamnose, identified by means of its osazone. Analyses of the kampherol thus obtained, m. p. $275-277^{\circ}$ (found, $C=63.01$; $H=3.68$ per cent), and its acetyl compound, m. p. 181° (found, $C=60.77$; $H=4.43$ per cent), were made for purposes of confirmation. By the method employed, 1.5 per cent of the glucoside was isolated, but considerably more of this is really present, as 2 per cent of an impure kampherol contaminated with a reddish brown substance, probably the so-called "indigo-brown," could be obtained by hydrolysing the aqueous extract of the leaf.

140. "1:3-Diphenylbarbituric Acid and some Coloured Derivatives. Synthesis of 1:3-Diphenyluric Acid." By MARTHA ANNIE WHITELEY.

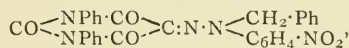
1:3-Diphenylbarbituric acid, $CO \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix} CH_2$, prepared by heating malonyl chloride and carbanilide or malonic acid, phosphorus oxychloride and carbanilide in chloroform solution, forms colourless prismatic needles and melts at 238° ; the dimethyl derivative, $CO \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix} CMe_2$, crystallises in colourless needles, melts at 230° , and sublimes at a slightly higher temperature; the isonitroso-derivative (diphenylvioluric acid), $CO \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix} C \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$, crystallises in colourless needles, melts and decomposes at 227° , and yields the red or violet salts characteristic of this type of compound; the potassium, aniline, and piperidine salts were prepared; the acetyl derivative, $C_{16}H_{10}O_3N_3 \cdot OAc$, crystallises in colourless prisms and melts at 245° . 1:3-Diphenyl-5-amino-barbituric acid (1:3-diphenyluramyl), obtained by reducing diphenylvioluric acid, forms colourless crystals, melts and decomposes at 195° , and condenses with potassium cyanate to form 1:3-diphenyl- ψ -uric acid, $CO \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix} CH \cdot NH \cdot CO \cdot NH_2$, which crystallises in colourless prisms, melts and decomposes at 217° , and on boiling with hydrochloric acid yields 1:3-diphenyluric acid, $\begin{smallmatrix} \text{NPh} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \\ | \quad \quad \quad || \\ \text{CO} \cdot \text{NPh} \cdot \text{C} \cdot \text{NH} \end{smallmatrix} CO$, which crystallises in colourless needles, softens at 238° , but does not melt at 306° .

1:3-Diphenylbarbituric acid condenses readily with aromatic aldehydes or diazonium chlorides, and the resulting compounds are of a bright yellow or orange colour. 5-Benzylidene-1:3-diphenylbarbituric acid, $CO \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix} C:CHPh$, forms pale yellow prismatic needles from most of the ordinary solvents, crystallises from acetone or ethyl acetate in a mixture of colourless and yellow needles, each form melting sharply at 214° , and yielding on reduction 5-benzyl-1:3-diphenylbarbituric acid; 5-cinnamylidene-1:3-diphenylbarbituric acid, $CO \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix} C:CH:CH:CHPh$, forms bright yellow needles and melts and decomposes at 268° . 1:3-Diphenylalloxanphenylhydrazone, $CO \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix} C:N:NHPh$, forms bright yellow needles and melts and decomposes

at 264° ; 1:3-Diphenylalloxan-p-nitrophenylhydrazone, $CO \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix} C:N:NH \cdot C_6H_4 \cdot NO_2$, forms well-developed orange prisms and melts at 274° ; 1:3-diphenylalloxan-benzyl-p-nitrophenylhydrazone,—



or—



from 5-benzyl-1:3-diphenylbarbituric acid and diazotised *p* nitraniline, crystallises in beautiful yellow prisms and melts and decomposes at 180° . Alloxanphenylmethylhydrazone, $CO \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} C:N:NMePh$, from alloxan and phenylmethylhydrazone, crystallises in brick-red hexagonal plates, which melt and decompose at $189-190^{\circ}$.

(To be continued).

NOTICES OF BOOKS.

German Grammar for Science Students. By W. A. OSBORNE, M.B., D.Sc., and ETHEL E. OSBORNE, M.Sc. London and New York: Whittaker and Co. 1906.

THE object of this grammar is to assist the student in acquiring such a knowledge of German as shall enable him to read articles and treatises on scientific subjects in that language. The authors have limited themselves to the production of a guide to the translation of German into English, and have introduced only such grammatical rules as are indispensable for the purpose. The method agrees closely with that adopted in the generality of elementary grammars, with the difference that the vocabulary consists chiefly of scientific words instead of those used in general conversation. The syntactical peculiarities of the language are explained as far as possible, and the later exercises contain some sentences of average difficulty, although this part of the book might with advantage be somewhat extended. Special stress is laid upon chemistry, and an appendix gives lists of words used in this and other sciences, with their English equivalents; these lists will be found very useful in supplementing a dictionary, and with the help of this book an average student ought rapidly to acquire a sufficient knowledge of German to enable him to read the language with comparative ease.

Preservatives in Food and Food Examination. By JOHN C. THRESH, M.D. (Vic.), D.Sc. (Lond.), F.I.C., and ARTHUR E. PORTER, M.D., M.A., (Cantab). London: J. and A. Churchill. 1906.

THE preservation of foods by various means is treated very fully in this book, and from the data at their disposal the authors conclude that the evils ascribed to the use of preservatives have been greatly exaggerated. Part I. opens with a discussion of methods of preserving, and in it chemical preservatives are criticised from the point of view of their applicability in different cases. In the second part the principal foods which are subjected to preservative processes are considered; for instance, milk, butter, alcoholic and other beverages; while Part III. deals with the addition of colouring matters to foods. The legal aspect of the question is then discussed at some length, while not the least valuable section of the book is that devoted to the description of methods of detecting and estimating impurities and adulterations. The report of the Departmental Committee appointed in 1899 by the President of the Local Government Board to inquire into the question is contained in an appendix, and there is also a short note on the law and practice in certain foreign countries and the colonies as to preservatives and colouring matters in food.

The book will be found of considerable value to the analytical chemist and medical officers of health. Those interested in the preparation of articles of food, and even the general public, might derive some benefit from its perusal.

A Handbook for Cane-sugar Manufacturers and their Chemists. By GUILFORD L. SPENCER, D.Sc. Fourth Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1906.

THE fourth edition of this book contains much new matter, and it now includes a description of the sugar manufacturing processes, with which the chemist should be familiar, while the analysis of the various products is carefully described, many valuable practical suggestions being interspersed throughout the text. The descriptions of the use of the polariscope are particularly full and clear, and even chemists with very little experience should find no difficulty in manipulating it if they follow exactly the author's directions. The method of analysis of molasses cattle-food is indicated, and a useful set of tables is given, including both those employed by general chemists and also those to which the sugar chemist has constantly to refer. The book will be found indispensable in sugar laboratories, the fourth edition being a great advance on those previously issued.

Water Softening and Treatment. By WILLIAM H. BOOTH. London: Archibald Constable and Co., Ltd. 1906.

THE author of this book is an acknowledged authority in the engineering world, and has, moreover, had much experience in the arrangement of water softening plant, so that he is well qualified to produce a comprehensive work on the subject. The book is intended for both steam users and dyers, and the first part of it gives a full account of the treatment of water by softening, oil separation, and filtering; the apparatus in general use for softening is described at some length, and the analysis of water is discussed; this seems unnecessary in a book of this kind, for it is a question that concerns the analytical chemist only. The remaining sections of the book deal with air-pumps, condensers and circulating pumps, feed heating, feed pumps, &c., and are mainly occupied with descriptions and plans of mechanical contrivances. The illustrations have been carefully prepared, and the uses of the various appliances are discussed from a practical point of view, the author giving his readers the full benefit of the experience he has acquired, besides drawing on many other authorities.

Die Elektrolyse Geschmolzener Salze. Dritter Teil: Elektromotorische Kräfte. ("The Electrolysis of Fused Salts. Part III.: Electromotive Forces"). By RICHARD LORENZ. Halle-a-S.: Wilhelm Knapp. 1906.

THE third part of this monograph deals with electromotive forces, and is no less valuable and complete than the two preceding volumes. Dr. Lorenz has collected his material with great care, and has enriched the book with useful practical suggestions for improving known processes or evolving fresh ones. Each section contains an historical introduction which gives in all cases an interesting and unbiassed account of the work of various investigators; the theory of the special branch treated in the section is then discussed, and researches on it are described. At the end of the book a section is devoted to the application of the theory of electrolytic dissociation to the fused and solid states, and after examining the support given to the theory by observations and facts, the author unhesitatingly declares for the existence of ions in the fused state. The production of this book undoubtedly marks a decided advance in our knowledge of the electrolysis of fused salts.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

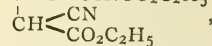
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 26, June 25, 1906.

Formation of Endothermic Combinations at High Temperatures.—M. Berthelot.—Hitherto no exact observations have been made to establish, either in fact or in principle, that very high temperatures are susceptible of causing a reversibility of chemical affinity by provoking the direct formation of endothermic combinations by simple heating, *i.e.*, without simultaneous employment of electrical or chemical energies.

Action of Water Vapour on Sulphides at a Red Heat. Production of Native Metals. Application to Volcanic Phenomena.—Armand Gautier.—The water vapour which is emitted at a red heat from deep crystalline rocks, such as granite, &c., on being liberated attacks the metallic portions of these rocks (especially their ferrous silicates), peroxidising these compounds and liberating the hydrogen, accompanied by other gases (carbonic oxide, carbonic acid, methane, nitrogen, &c.). This oxidation of the silicates and of carbonic oxide by water vapour leads the author to make a complete investigation of the action of water vapour at a red heat—(1) On iron sulphides; (2) on metallic sulphides which are not decomposed by water; (3) on sulphuretted hydrogen.

Condensation of $\beta\beta$ -Dimethylglycidic Ether with Sodium Malonic Ether. Synthesis of Terebic and Pyroterebic Acids.—A. Haller and G. Blanc.—In order to prepare the cyano-ether,



the authors condense dimethylglycidic ether with sodium cyanacetic ether. The reaction is complete after several hours' heating on a water-bath. The results were not good, better ones being obtained by using malonic ether. After various processes, 4-methyl-2,3-dicarboxethyl pentanolate-4 is formed as the final product, and on boiling with hydrochloric acid this ether lactone gives quantitatively an acid scarcely soluble in water and melting at 175°, corresponding to the formula $\text{C}_7\text{H}_{10}\text{O}_4$, and known as terebic acid. From this its isomer, pyroterebic acid, can be prepared by the action of heat.

Heat of Formation of Carbonylferrohydrocyanic Acid.—J. A. Muller.—The heat of formation of carbonylferrohydrocyanic acid from its elements can only be deduced from its heat of combustion, because the method of synthesis from ferrocyanides does not lend itself to any other method. The author finds the number 3444 cal. as a mean of seven experiments.

Cathodic Phosphorescence of Europium Diluted with Lime. Examination of the Triple Phosphorescent System, Lime—Gadolinia—Europia.—G. Urbain.—Whilst investigating the phosphorescence of successive fractions of europium-ferrous earths diluted with lime, the author observed a new phenomenon, which he is able to reproduce synthetically, and which shows how the radiation emitted in phosphorescence is susceptible of being modified under the influence of relatively weak chemical action. The spectrum lines are described, and the system lime—gadolinia—europia examined.

Variations in State shown by Amorphous Carbon under the Influence of a Rapid Variation of Temperature.—O. Manville.—The author's experiments show that the state of amorphous carbon varies sensibly with the temperature. For the same temperature, *t*, comprised between the limits T_0 and T_1 the state of the carbon is not the same when *t* is proportional to the phase of heating or to the phase of cooling. Finally, there exists a tempera-

ture, t , in the heating phase, and a temperature, t' , different from t , in the cooling phase for which the state of the carbon gives with the same current of oxygen the same reaction velocity.

Double Sulphate of Iridium and Potassium.—Marcel Delépine.—The author investigates the complex character of the double sulphate of iridium and potassium, $\text{Ir}_2(\text{SO}_4)_3 + 3\text{K}_2\text{SO}_4$.

Silicones.—M. Boudouard.—The silicones are the products obtained by the action of hydrochloric acid on certain metallic silicides, and they have the property of being slowly decomposed by the action of water, with evolution of hydrogen. These substances represent examples of substances comparable with the triple derivatives of carbon with total substitution of silicon for the carbon. Those prepared by the author can be considered as mixtures of siliciformic anhydride and silicoxalic hydrate in varying proportions. Perfectly definite compounds cannot be prepared, on account of the difficulty of attacking the silicides and of the prolonged contact of the silicone, acid, and water which is the immediate consequence of it.

Crystallography of Iron.—F. Osmond and G. Cartaud.—The authors continue their researches on the crystalline forms obtained when ferrous chloride is reduced at different temperatures by hydrogen or zinc vapour. The distinctive crystalline characteristics of the three varieties of iron so prepared are given in a table.

Action of Oxygen on Rubidium-ammonium.—E. Rengade.—The author investigates the action of oxygen on rubidium-ammonium, and finds that the three metals potassium, caesium, and rubidium, when dissolved in excess of liquefied ammonia, give, in presence of oxygen, first a white binoxide, and finally a yellow tetroxide. The potassium and the caesium give, besides, a very dark trioxide, which is not found with rubidium. These oxides in order to be pure should be formed very rapidly; a slow oxidation gives a binoxide mixed with hydride and amide, and consequently superior oxides mixed with the products of oxidation of the amide, *i.e.*, nitrite and nitrate.

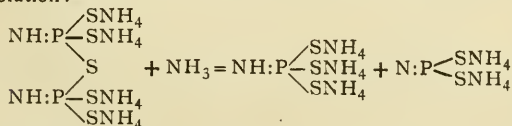
Pyrazolones. New Methods of Synthesis.—Ch. Moureu and I. Lazennec.—The authors find a new method of synthesis of pyrazolones by making the hydrazines act on the β -oxalcoyl-acrylic ethers.

Phenyl Migrations in Halohydrines and α -Glycols.—M. Tiffeneau.

Cinnaménylparaconic Acid.—J. Bougault.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 9, 1906.

Reaction between Phosphorus Pentasulphide and Ammonia.—Alfred Stock.—If gaseous ammonia is led over phosphorus pentasulphide at a low temperature a yellow substance, $\text{P}_2\text{S}_5 \cdot 6\text{NH}_3$, is formed. This substance, which can also be made by dissolving the sulphide in liquid ammonia and evaporating off the excess of ammonia, gradually loses its colour when an ammoniacal solution is allowed to stand for some time, leaving on evaporation $\text{P}_2\text{S}_5 \cdot 7\text{NH}_3$. This latter is a mixture of two ammonium salts, from which triammonium-imido-tri-thiophosphate separates out in crystals after about a day, while diammonium nitrilo dithiophosphate remains in solution:—



Ammonium imido-tri-thiophosphate is very readily attacked by water, and from it a series of new products can be obtained.

Simple and Sensitive Thermometer for Low Temperatures.—Alfred Stock and Carl Nielsen.—In this thermometer the tension which a small quantity of liquid oxygen possesses at the temperature to be measured is determined. The thermometer consists essentially of an oxygen holder of about 25 c.c. capacity, connected with a mercury manometer. The tension of liquid oxygen at various temperatures is known fairly accurately, and the tensions at the lowest temperatures may be obtained from a tension curve. Temperatures of from -183° to -200° can be quickly and accurately determined with this instrument, and differences of $1/100^\circ$ can be detected, while other gases can be used instead of oxygen for different ranges of temperature.

Employment of Sodium Hydrosulphite in Gas Analysis.—Hartwig Franzen.—The author has investigated the use of sodium hydrosulphite for the absorption of oxygen in gas analysis, and has found that its use presents many advantages. The solution is prepared by dissolving 50 grms. of the salt in 250 c.c. of water and adding 40 c.c. of caustic soda solution (500 grms. sodium hydroxide in 700 c.c. of water). According to the equation $\text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2\text{O} + \text{O} = 2\text{NaHSO}_3$ 1 gm. of the salt absorbs 64 c.c. of oxygen. Therefore 1 c.c. of the above solution absorbs 10.7 c.c. of oxygen. It is much cheaper than pyrogallol, and the absorption proceeds as rapidly at low as at higher temperatures. It can be used to analyse gases containing the oxides of carbon, and many substances which hinder an oxidation of phosphorus have no effect on sodium hydrosulphite.

MISCELLANEOUS.

Institute of Chemistry of Great Britain and Ireland.—*Pass List of the July Examinations.*—Of fourteen candidates who entered for the Intermediate Examination, the following nine passed: L. C. W. Bonacina; W. R. S. Ladell; D. J. Law; W. M. Seaber, B.Sc. (Lond.); P. Stutfield; J. M. Weir, M.A., B.Sc. (St. Andrews); W. A. Whatmough; J. M. Wilkie, B.Sc. (Lond.); and C. H. Wright, B.A. (Cantab). In the Final Examination for the Associateship (A.I.C.), of three examined in the branch of Mineral Chemistry, two passed: J. W. Agnew and I. M. Heilbron. Of three in the branch of Organic Chemistry, two passed: R. Le Rossignol, B.Sc. (Lond.), and G. W. Monier-Williams, M.A. (Oxon.), Ph.D (Freiburg). Of eight who entered in the branch of the Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following six passed: J. G. Annan, B.Sc. (Lond.); C. T. Bennett, B.Sc. (Lond.); G. W. Glen; F. W. Harris; E. H. Merritt, B.Sc. (Lond.); and F. Tattersfield. The Examiners in Chemistry were Mr. W. W. Fisher, M.A. (Oxon.), F.I.C., and Dr. G. G. Henderson, M.A. (Glasgow), F.I.C. The Examination in Therapeutics, Pharmacology, and Microscopy was conducted by Dr. F. Gowland Hopkins, M.A. (Cantab), F.R.S., F.I.C.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Heat of Combustion of Iron Sulphide.—Will some correspondent favour me with a reply to the following question:—What is the heat of combustion of iron sulphide, FeS_2 ?—A. W.

Uranium.—We wish to obtain some particulars concerning uranium salts:—(1) As to its character, composition, and properties; (2) approximate present market value per lb., or per ton; (3) statistics as to the quantities at present available in the different markets. If any correspondents are able to furnish us with any information concerning the above, we should be extremely grateful.—A. B. & Co.

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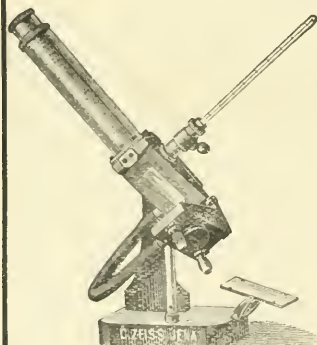
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THE CHEMICAL NEWS.

VOL. XCIV., No. 2436.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

YORK, 1906.

INAUGURAL ADDRESS OF THE PRESIDENT,
Prof. E. RAY LANKESTER, M.A., LL.D., D.Sc., F.R.S.,
F.L.S., Director of the Natural History Departments
of the British Museum.

MY LORDS, LADIES, AND GENTLEMEN,—It is, first of all, my privilege to thank you for the distinguished honour you have done me in electing me President of this great scientific Association—an honour which is enhanced by the fact that our meeting this year is once more held in the venerable city of York, in which seventy-five years ago the British Association for the Advancement of Science held its first meeting.

It is a great pleasure to me to convey to the Lord Mayor and the dignitaries and citizens of York your hearty thanks for the invitation to meet this year in their city. It seems to have become a custom that the Association should be invited at regular intervals to assemble in the city where it took birth, and to note the progress made in the objects for the furtherance of which it was founded. A quarter of a century ago we met here under the presidency of that versatile leader in public affairs—Sir John Lubbock, now Lord Avebury. That occasion was the jubilee—the fiftieth anniversary—of the Association.

Lord Avebury on that occasion gave as his presidential address a survey of the progress of science during the fifty years of the Association's existence. He had a wonderful story to tell, and told it with a fulness which was only possible to one of his wide range of knowledge and keen interest in the various branches of science. If I venture on the present occasion to say a few words as to the great features in the progress of our knowledge of Nature during the last twenty-five years, it will be readily understood that the mere volume of new knowledge to be surveyed has become so vast that a full and detailed statement such as that which Lord Avebury placed before the Association at its jubilee is no longer possible in a single address delivered from the President's chair.

Let me ask you before we go further to take for a few moments a more personal retrospect, and to think of the founders of this Association, then of the great workers in science who were still alive in 1881 when last we met here, and have since gone from among us, leaving their great deeds and their noble enthusiasm to inspire now and for all future time those who have vowed themselves to the advancement of science in this realm of Britain.

There must be some here who had the privilege of personal acquaintance with several of the men who founded this Association in York seventy-five years ago. I myself knew Professor John Phillips, Sir Charles Lyell, Sir Roderick Murchison, Sir David Brewster, Dr. Whewell, and Mr. Harcourt, of Nuneham. All these fathers of our Association had passed away before our last meeting in York. And now, in the quarter of a century which has rolled by and brought us here again, we have lost many who took an active part in its annual meetings, and were familiar figures in the scientific world of the later Victorian period. Huxley and Tyndall, Spottiswoode and Cayley, Owen and Flower, Williamson and Frankland, Falconer and Busk, Prestwich and Godwin Austen, Rolleston and Henry Smith, Stokes and Tait, and many others are in that list, including one whose name was, and is, more

often heard in our discussions than any other, though he himself never was able to join us—I mean Charles Darwin. Happily some of the scientific veterans of the nineteenth century are still living, if not with us in York. Sir Joseph Hooker, who visited the Antarctic with Ross in 1839, is still hale and hearty, and so are Alfred Russel Wallace, Lord Kelvin, Sir William Huggins, and many others who were already veteran leaders in scientific investigation when last we visited York; they are still active in thought, observation, and experiment.

In attempting to give an outline of the advancement of science in the past twenty-five years I think it is necessary to distinguish two main kinds of advancement, both of which our founders had in view. Francis Bacon gave the title "Advancement of Learning" to that book in which he explained not merely the methods by which the increase of knowledge was possible, but advocated the promotion of knowledge to a new and influential position in the organisation of human society. His purpose, says Dean Church, was "to make knowledge really and intelligently the interest, not of the school or the study or the laboratory only, but of society at large." This is what our founders also intended by their use of the word "advancement." So that in surveying the advancement of science in the past quarter of a century we of the British Association must ask not only what are the new facts discovered, the new ideas and conceptions which have come into activity, but what progress has science made in becoming really and intelligently the interest of society at large. Is there evidence that there is an increase in the influence of science on the lives of our fellow-citizens and in the great affairs of the State? Is there an increased provision for securing the progress of scientific investigation in proportion to the urgency of its need or an increased disposition to secure the employment of really competent men trained in scientific investigation for the public service?

I. *The Increase of Knowledge in the Several Branches of Science.*

The boundaries of my own understanding and the practical consideration of what is appropriate to a brief address must limit my attempt to give to the general public who follow with friendly interest our proceedings some presentation of what has been going on in the workshops of science in this last quarter of a century. My point of view is essentially that of the naturalist, and in my endeavour to speak of some of the new things and new properties of things discovered in recent years I find it impossible to give any systematic or detailed account of what has been done in each division of science. All that I can attempt is to mention some of the discoveries which have aroused my own interest and admiration. I feel, indeed, that it is necessary to ask your forbearance for my presumption in daring to speak of so many subjects in which I cannot claim to speak as an authority, but only as a younger brother full of fraternal pride and sympathy in the glorious achievements of the great experimentalists and discoverers of our day. The duty of attempting some indication of their work is placed upon me as your President, and it is for my effort to discharge that duty that I ask your generous consideration.

As one might expect, the progress of the knowledge of nature (for it is to that rather than to the historical, moral, and mental sciences that English-speaking people refer when they use the word "science") has consisted, in the last twenty-five years, in the amplification and fuller verification of principles and theories already accepted, and in the discovery of hitherto unknown things which either have fallen into place in the existing scheme of each science or have necessitated new views, some not very disturbing to existing general conceptions, others of a more startling and, at first sight, disconcerting character. Nevertheless, I think I am justified in saying that, exciting and of entrancing interest as have been some of the discoveries of the past few years, there has been nothing to lead us to conclude that we have been on the wrong path—nothing

which is really revolutionary; that is to say, nothing which cannot be accepted by an intelligible modification of previous conceptions. There is, in fact, continuity and consistency in the realm of science. Whilst some persons have been inclined to regard the discoveries of the last few years as a complete revolution, and to assert that the old conceptions are now obsolete, others have asserted, on the contrary, that the new discoveries—such as those relating to the X-rays and to radium—are so inconsistent with previous knowledge as to shake the foundations of science, and to justify a belief in any and every absurdity of an unrestrained fancy. These two reciprocally destructive accusations are due to a class of persons who must be described as the enemies of science. Whether their attitude is due to ignorance or traditions of self-interest, such persons exist; and it is one of the objects of this Association to combat their assertions and to demonstrate, by the discoveries announced at its meetings and the consequent orderly building up of the great fabric of "natural knowledge," that Science has not come to the end of her work—has, indeed, only as yet given mankind a foretaste of what she has in store for it—that her methods and her accomplished results are sound and trustworthy, serving with perfect adaptability for the increase of true discovery, and the expansion and development of those general conceptions of the processes of nature at which she aims.

New Chemical Elements.—There can be no doubt that the past quarter of a century will stand out for ever in human history as that in which new chemical elements, not of an ordinary type, but possessed of truly astounding properties, were made known with extraordinary rapidity and sureness of demonstration. Interesting as the others are, it is the discovery of radio-activity and of the element radium which so far exceeds all others in importance that we may well account it a supreme privilege that it has fallen to our lot to live in the days of this discovery. No single discovery ever made by the searchers of nature can approach that of radio-activity in respect of the amount of the properties of matter which it has opened to us. A new conception of the structure of matter has been established, and a new method of investigation has been found, and a new conception of the nature of matter has been brought out, and grows out of, and justifies the older schemes which our previous knowledge has formulated.

Before saying more of radio-activity, which is apt to eclipse in interest every other topic of discourse, I must recall to you the discovery of the five inert gaseous elements by Rayleigh and Ramsay, which belongs to the period on which we are looking back. It was found that nitrogen obtained from the atmosphere invariably differed in weight from nitrogen obtained from one of its chemical combinations; and thus the conclusion was arrived at by Rayleigh that a distinct gas is present in the atmosphere, to the extent of 1 per cent, which had hitherto passed for nitrogen. This gas was separated, and to it the name argon (the lazy one) was given, on account of its incapacity to combine with any other element. Subsequently, this argon was found by Ramsay to be itself impure, and from it he obtained three other gaseous elements equally inert: namely, neon, krypton, and xenon. These were all distinguished from one another by the spectrum, the sign-manual of an element given by the light emitted in each case by the gas when in an incandescent condition. A fifth inert gaseous element was discovered by Ramsay as a constituent of certain minerals which was proved by its spectrum to be identical with an element discovered twenty-five years ago by Sir Norman Lockyer in the atmosphere of the sun, where it exists in enormous quantities. Lockyer had given the name (helium) to this new solar element, and Ramsay thus found it locked up in certain rare minerals in the crust of the earth.

But by helium we are led back to radium, for it has been found only two years ago by Ramsay and Soddy that helium is actually formed by a gaseous emanation from radium. Astounding as the statement seems, yet that is one of the many unprecedented facts which recent study

has brought to light. The alchemist's dream is, if not realised, at any rate justified. One element is actually under our eyes converted into another; the element radium decays into a gas which changes into another element—namely, helium.

Radium, this wonder of wonders, was discovered owing to the study of the remarkable phosphorescence, as it is called—the glowing without heat—of glass vacuum-tubes through which electric currents are made to pass. Crookes, Lenard, and Röntgen each played an important part in this study, showing that peculiar rays or linear streams of at least three distinct kinds are set up in such tubes—rays which are themselves invisible, but have the property of making glass or other bodies which they strike glow with phosphorescent light. The celebrated Röntgen rays make ordinary glass give out a bright green light; but they pass through it, and cause phosphorescence outside in various substances, such as barium platino-cyanide, calcium tungstate, and many other such salts; they also act on a photographic plate and discharge an electrified body such as an electroscope. But the most remarkable feature about them is their power of penetrating substances opaque to ordinary light. They will pass through thin metal plates or black paper or wood, but are stopped by more or less dense material. Hence it has been possible to obtain "shadow pictures" or skiagraphs by allowing the invisible Röntgen rays to pass through a limb or even a whole animal, the denser bone stopping the rays, whilst the skin, flesh, and blood let them through. They are allowed to fall (still invisible) on to a photographic plate, when a picture like an ordinary permanent photograph is obtained by their chemical action, or they may be made to exert their phosphorescence-producing power on a glass plate covered with a thin coating of a phosphorescent salt such as barium platino-cyanide, when a temporary picture in light and shade is seen.

The rays discovered by Röntgen were known as the X-rays, because their exact nature was unknown. Other rays studied in the electrified vacuum-tubes are known as cathode rays, or radiant corpuscles, and, others, again, as the Lenard rays.

It occurred to M. Henri Becquerel, as he himself tells us, to inquire whether other phosphorescent bodies besides the glowing vacuum-tubes of the electrician's laboratory can emit penetrating rays like the X-rays. I say "other phosphorescent bodies," for this power of glowing without heat—of giving out, so to speak, cold light—is known to be possessed by many mineral substances. It has become familiar to the public in the form of "phosphorescent paint," which contains sulphide of calcium, a substance which shines in the dark after exposure to sunlight—that is to say, is phosphorescent. Other sulphides and the minerals fluor-spar, apatite, some gems, and, in fact, a whole list of substances have, under different conditions of treatment, this power of phosphorescence or shining in the dark without combustion or chemical change. All, however, require some special treatment, such as exposure to sunlight or heat or pressure, to elicit the phosphorescence, which is of short duration only. Many of the compounds of a somewhat uncommon metallic element, called uranium, used for giving a fine green colour to glass, are phosphorescent substances, and it was, fortunately, one of them which Henri Becquerel chose for experiment. Henri Becquerel is professor in the Jardin des Plantes of Paris; his laboratory is a delightful old-fashioned building, which had for me a special interest and sanctity when, a few years ago, I visited him there, for, a hundred years before, it was the dwelling-house of the great Cuvier. Here Henri Becquerel's father and grandfather—men renowned throughout the world for their discoveries in mineralogy, electricity, and light—had worked, and here he had himself gone almost daily from his earliest childhood. Many an experiment bringing new knowledge on the relations of light and electricity had Henri Becquerel carried out in that quiet old-world place before the day on

which, about twelve years ago, he made the experimental inquiry, Does uranium give off penetrating rays like Röntgen's rays? He wrapped a photographic plate in black paper, and on it placed and left lying there for twenty-four hours some uranium salt. He had placed a cross, cut out in thin metallic copper, under the uranium powder, so as to give some shape to the photographic print should one be produced. It was produced. Penetrating rays were given off by the uranium: the black paper was penetrated, and the form of the copper cross was printed on a dark ground. The copper was also penetrated to some extent by the rays from the uranium, so that its image was not left actually white. Only one step more remained before Becquerel made his great discovery. It was known, as I stated just now, that sulphide of calcium and similar substances become phosphorescent when exposed to sunlight, and lose this phosphorescence after a few hours. Becquerel thought at first that perhaps the uranium acquired its power similarly by exposure to light; but very soon, by experimenting with uranium long kept in the dark, he found that the emission of penetrating rays, giving photographic effects, was produced spontaneously. The emission of rays by this particular fragment of uranium has shown no sign of diminution since this discovery. The emission of penetrating rays by uranium was soon found to be independent of its phosphorescence. Phosphorescent bodies, as such, do not emit penetrating rays. Uranium compounds, whether phosphorescent or not, emit, and continue to emit, these penetrating rays, capable of passing through black paper and metallic copper. They do not derive this property from the action of light or any other treatment. The emission of these rays discovered by Becquerel is a new property of matter. It is called "radio-activity," and the rays are called Becquerel rays.

From this discovery by Becquerel to the detection and separation of the new element radium is an easy step in thought, though one of enormous labour and difficulty in practice. Professor Pierre Curie (whose name I cannot mention without expressing the grief with which we all heard in last April of the sad accident by which his life was taken) and his wife, Madame Skłodowska Curie, incited by Becquerel's discovery, examined the ore called pitchblende which is worked in mines in Bohemia and is found also in Cornwall. It is the ore from which all commercial uranium is extracted. The Curies found that pitchblende has a radio-activity four times more powerful than that of metallic uranium itself. They at once conceived the idea that the radio-activity of the uranium salts examined by Becquerel is due not to the uranium itself, but to another element present with it in variable quantities. This proved to be in part true. The refuse of the first processes by which in the manufacturer's works the uranium is extracted from its ore, pitchblende, was found to contain four times more of the radio-active matter than does the pure uranium. By a long series of fusions, solutions, and crystallisations the Curies succeeded in "hunting down," as it were, the radio-active element. The first step gave them a powder mixed with barium chloride, and having 2000 times the activity of the uranium in which Becquerel first proved the existence of the new property—radio-activity. Then step by step they purified it to a condition 10,000 times, then to 100,000 times, and, finally, to the condition of a crystalline salt having 1,800,000 times the activity of Becquerel's sample of uranium. The purification could go no further, but the extraordinary minuteness of the quantity of the pure radio-active substance obtained, and the amount of labour and time expended in preparing it, may be judged of from the fact that of one ton of the pitchblende ore submitted to the process of purification only the hundredth of a gram—the one-seventh of a grain—remained.

The amount of radium in pitchblende is one ten-millionth per cent; rarer than gold in sea-water. The marvel of this story and of all that follows consists largely in the skill and accuracy with which our chemists and physicists have learnt to deal with such infinitesimal quantities, and the

gigantic theoretical results which are securely posed on this pin-point of substantial matter.

The Curies at once determined that the minute quantity of colourless crystals they had obtained was the chloride of a new metallic element with the atomic weight 225, to which they gave the name radium. The proof that radium is an element is given by its "sign-manual"—the spectrum which it shows to the observer when in the incandescent state. It consists of six bright lines and three fainter lines in the visible part of the spectrum, and of three very intense lines in the ultra-violet (invisible) part. A very minute quantity is enough for this observation; the lines given by radium are caused by no other known element in heaven or earth. They prove its title to be entered on the roll-call of elements.

The atomic weight was determined in the usual way by precipitating the chlorine in a solution of radium chloride by means of silver. None of the precious element was lost in the process, but the Curies never had enough of it to venture on any attempt to prepare pure metallic radium. This is a piece of extravagance no one has yet dared to undertake. Altogether, the Curies did not have more than some four or five grains of chloride of radium to experiment with, and the total amount prepared and now in the hands of scientific men in various parts of the world probably does not amount to more than sixty grains at most. When Professor Curie lectured on radium four years ago at the Royal Institution in London he made use of a small tube an inch long and of one-eighth bore, containing nearly the whole of his precious store, wrenched by such determined labour and consummate skill from tons of black shapeless pitchblende. On his return to Paris he was one day demonstrating in his lecture-room with this precious tube the properties of radium, when it slipped from his hand, broke, and scattered far and wide the most precious and magical powder ever dreamed of by alchemist or artist of romance. Every scrap of dust was immediately and carefully collected, dissolved, and re-crystallised, and the disaster averted with a loss of but a minute fraction of the invaluable product.

Thus, then, we have arrived at the discovery of radium—the new element endowed in an intense form with the new property "radio-activity" discovered by Becquerel. The wonder of this powder, incessantly and without loss, under any and all conditions pouring forth by virtue of its own intrinsic property powerful rays capable of penetrating opaque bodies, and of exciting phosphorescence and acting on photographic plates, can perhaps be realised when we reflect that it is as marvellous as though we should dig up a stone which without external influence or change, continually poured forth light or heat, manufacturing both in itself, and not only continuing to do so without appreciable loss or change, but necessarily having always done so for countless ages whilst sunk beyond the ken of man in the bowels of the earth.

Wonderful as the story is, so far it is really simple and commonplace compared with what yet remains to be told. I will only barely and abruptly state the fact that radio-activity has been discovered in other elements, some very rare, such as actinium and polonium; others more abundant and already known, such as thorium and uranium, though their radio-activity was not known until Becquerel's pioneer-discovery. It is a little strange and no doubt significant that, after all, pure uranium is found to have a radio-activity of its own, and not to have been altogether usurping the rights of its infinitesimal associate.

The wonders connected with radium really begin when the experimental examination of the properties of a few grains is made. What I am saying here is not a systematic technical account of radium; so I shall venture to relate some of the story as it impresses me.

Leaving aside for a moment what has been done in regard to the more precise examination of the rays emitted by radium, the following astonishing facts have been found out in regard to it:—1. If a glass tube containing radium is much handled or kept in the waistcoat pocket, it pro-

duces a destruction of the skin and flesh over a small area—in fact, a sore place. 2. The smallest trace of radium brought into a room where a charged electroscope is present, causes the discharge of the electroscope. So powerful is this electrical action of radium that a very sensitive electrometer can detect the presence of a quantity of radium five hundred thousand times more minute than that which can be detected by the spectroscopic (that is to say, by the spectroscopic examination of a flame in which minute traces of radium are present). 3. Radium actually realises one of the properties of the hypothetical stone to which I compared it giving out light and heat. For it does give out heat which it makes itself incessantly and without appreciable loss of substance or energy ("appreciable" is here an important qualifying term). It is also faintly self-luminous. Fairly sensitive thermometers show that a few granules of radium salt have always a higher temperature than that of surrounding bodies. Radium has been proved to give out enough heat to melt rather more than its own weight of ice every hour; enough heat in one hour to raise its own weight of water from the freezing-point to the boiling-point. After a year and six weeks a gramme of radium has emitted enough heat to raise the temperature of a thousand kilograms of water one degree. And this is always going on. Even a small quantity of radium diffused through the earth will suffice to keep up its temperature against all loss by radiation! If the sun consists of a fraction of 1 per cent of radium this will account for and make good the heat that is annually lost by it.

This is a tremendous fact, upsetting all the calculations of physicists as to the duration in past and future of the sun's heat and the temperature of the earth's surface. The geologists and the biologists have long contended that some thousand million years must have passed during which the earth's surface has presented approximately the same conditions of temperature as at present, in order to allow time for the evolution of living things and the formation of the aqueous deposits of the earth's crust. The physicists, notably Professor Tait and Lord Kelvin, refused to allow more than ten million years (which they subsequently increased to a hundred million)—basing this estimate on the rate of cooling of a sphere of the size and composition of the earth. They have assumed that its material is self-cooling. But, as Huxley pointed out, mathematics will not give a true result when applied to erroneous data. It has now, within these last five years, become evident that the earth's material is *not* self-cooling, but, on the contrary, self heating. And away go the restrictions imposed by physicists on geological time. They now are willing to give us not merely a thousand million years, but as many more as we want.

And now I have to mention the strangest of all the proceedings of radium—a proceeding in which the other radioactive bodies, actinium and thorium, resemble it. This proceeding has been entirely Rutherford's discovery in Canada, and his name must be always associated with it. Radium (he discovered) is continually giving off, apart from and in addition to the rectilinear darting rays of Becquerel—an "emanation"—a gaseous "emanation." This "emanation" is radio-active—that is, gives off Becquerel rays—and deposits "something" upon bodies brought near the radium, so that they become radio-active, and remain so for a time after the radium is itself removed. This emanation is always being formed by a radium salt, and may be most easily collected by dissolving the salt in water, when it comes away with a rush, as a gas. Sixty milligrams of bromide of radium yielded to Ramsay and Soddy 0.124 (or about $\frac{1}{8}$) of a cubic millimetre of this gaseous emanation. What is it? It cannot be destroyed or altered by heat or by chemical agents; it is a heavy gas, having a molecular density of 100, and it can be condensed to a liquid by exposing it to the great cold of liquid air. It gives a peculiar spectrum of its own, and is probably a hitherto unknown inert gas—a new element similar to argon. But this by no means completes its history, even so far as experiments have as yet gone. The radium

emanation decays, changes its character altogether, and loses half its radio-activity every four days. Precisely at the same rate as it decays the specimen of radium salt from which it was removed forms a new quantity of emanation, having just the amount of radio-activity which has been lost by the old emanation. All is not known about the decay of the emanation, but one thing is absolutely certain, having first been discovered by Ramsay and Soddy and subsequently confirmed by independent experiment by Madame Curie. It is this: After being kept three or four days the emanation becomes, in part at least, converted into helium—the light gas (second only in the list of elements to hydrogen), the gas found twenty-five years ago by Lockyer in the sun, and since obtained in some quantities from rare radio-active minerals by Ramsay! The proof of the formation of helium from the radium emanation is, of course, obtained by the spectroscopic, and its evidence is beyond assail. Here, then, is the partial conversion or decay of one element, radium, through an intermediate stage into another. And not only that, but if, as seems probable, the presence of helium indicates the previous presence of radium, we have the evidence of enormous quantities of radium in the sun, for we know helium is there in vast quantity. Not only that, but inasmuch as helium has been discovered in most hot springs and in various radio-active minerals in the earth, it may be legitimately argued that no inconsiderable quantity of radium is present in the earth. Indeed, it now seems probable that there is enough radium in the sun to keep up its continual output of heat, and enough in the earth to make good its loss of heat by radiation into space, for an almost indefinite period. Other experiments of a similar kind have rendered it practically certain that radium itself is formed by a somewhat similar transformation of uranium, so that our ideas as to the permanence and immutability on this globe of the chemical elements are destroyed, and must give place to new conceptions. It seems not improbable that the final product of the radium emanation after the helium is removed is or becomes the metal lead!

It must be obvious from all the foregoing that radium is very slowly, but none the less surely, destroying itself. There is a definite loss of particles which, in the course of time, must lead to the destruction of the radium, and it would seem that the large new credit on the bank of time given to biologists in consequence of its discovery has a definite, if remote, limit. With the quantities of radium at present available for experiment, the amount of loss of particles is so small, and the rate so slow, that it cannot be weighed by the most delicate balance. Nevertheless, it has been calculated that radium will transform half of itself in about fifteen hundred years, and unless it were being produced in some way all of the radium now in existence would disappear much too soon to make it an important geological factor in the maintenance of the earth's temperature. As a reply to this depreciatory statement we have the discovery by Rutherford and others that radium is continually being formed afresh, and from that particular element in connection with which it was discovered, namely, uranium. Hypotheses and experiments as to the details of this process are at this moment in full swing, and results of a momentous kind, involving the building-up of an element with high atomic weight by the interaction of elements with a lower atomic weight are thought by some physicists to be not improbable in the immediate future.

The delicate electric test for radio-activity has been largely applied in the last few years to all sorts and conditions of matter. As a result it appears that the radium emanation is always present in our atmosphere; that the air in caves is especially rich in it, as are underground waters. Tin-foil, glass, silver, zinc, lead, copper, platinum, and aluminium are, all of them, slightly radio-active. The question has been raised whether this widespread radio-activity is due to the wide dissemination of infinitesimal quantities of strong radio-active elements, or whether it is the natural intrinsic property of all matter to emit Becquerel rays. This is the immediate subject of research,

Over and above the more simply appreciable facts which I have thus narrated, there comes the necessary and difficult enquiry—What does it all mean? What are the Becquerel rays of radio-activity? What must we conceive to be the structure and mechanism of the atoms of radium and allied elements, which can not only pour forth ceaseless streams of intrinsic energy from their own isolated substance, but are perpetually, though in infinitesimal proportions, changing their elemental nature spontaneously, so as to give rise to other atoms which we recognise as other elements?

I cannot venture as an expositor into this field. It belongs to that wonderful group of men, the modern physicists, who with an almost weird power of visual imagination combine the great instrument of exact statement and mental manipulation called mathematics, and possess an ingenuity and delicacy in appropriate experiment which must fill all who even partially follow their triumphant handling of nature with reverence and admiration. Such men now or recently among us are Kelvin, Clerk Maxwell, Crookes, Rayleigh, and J. J. Thomson.

Becquerel showed early in his study of the rays emitted by radium that some of them could be bent out of their straight path by making them pass between the poles of a powerful electro-magnet. In this way have finally been distinguished three classes of rays given off by radium:—(1) the α -rays, which are only slightly bent, and have little penetrative power; (2) the β -rays, easily bent in a direction opposite to that in which the α -rays bend, and of considerable penetrative power; (3) the γ -rays, which are absolutely unbendable by the strongest magnetic force, and have an extraordinary penetrative power, producing a photographic effect through a foot thickness of solid iron.

The α -rays are shown to be streams of tiny bodies positively electrified, such as are given off by gas flames and red-hot metals. The particles have about twice the mass of a hydrogen atom, and they fly off with a velocity of 20,000 miles a second; that is, 40,000 times greater than that of a rifle bullet. The heat produced by radium is ascribed to the impact of these particles of the α -rays.

The β -rays are streams of corpuscles similar to those given off by the cathode in a vacuum tube. They are charged with negative electricity and travel at the velocity of 100,000 miles a second. They are far more minute than the α particles. Their mass is equal to the one-thousandth of a hydrogen atom. They produce the major part of the photographic and phosphorescent effects of the radium rays.

The γ -rays are apparently the same, or nearly the same, thing as the X-rays of Röntgen. They are probably not particles at all, but pulses or waves in the ether set up during the ejection of the corpuscles which constitute the β -rays. They produce the same effects in a much smaller degree as do the β -rays, but are more penetrating.

The kind of conceptions to which these and like discoveries have led the modern physicist in regard to the character of that supposed unbreakable body—the chemical atom—the simple and unaffected friend of our youth—are truly astounding. But I would have you notice that they are not destructive of our previous conceptions, but rather elaborations and developments of the simpler views, introducing the notion of structure and mechanism, agitated and whirling with tremendous force, into what we formerly conceived of as homogeneous or simply built-up particles, the earlier conception being not so much a positive assertion of simplicity as a non-committal expectant formula awaiting the progress of knowledge and the revelations which are now in our hands.

As I have already said, the attempt to show in detail how the marvellous properties of radium and radio-activity in general are thus capable of a pictorial or structural representation is beyond the limits both of my powers and the time allowed me; but the fact that such speculations furnish a scheme into which the observed phenomena can be fitted is what we may take on the authority of the physicists and chemists of our day.

Intimately connected with all the work which has been done in the past twenty-five years in the nature and possible transformations of atoms is the great series of investigations and speculations on astral chemistry and the development of the chemical elements which we owe to the unremitting labour during this period of Sir Norman Lockyer.

Wireless Telegraphy.—Of great importance has been the whole progress in the theory and practical handling of electrical phenomena of late years. The discovery of the Hertzian waves and their application to wireless telegraphy is a feature of this period, though I may remind some of those who have been impressed by these discoveries that the mere fact of electrical action at a distance is that which hundreds of years ago gave to electricity its name. The power which we have gained of making an instrument oscillate in accordance with a predetermined code of signalling, although detached and a thousand miles distant, does not really lend any new support to the notion that the old-time beliefs of thought-transference and second sight are more than illusions based on incomplete observation and imperfect reasoning. For the important factors in such human intercourse—namely, a signalling-instrument and a code of signals—have not been discovered, as yet, in the structure of the human body, and have to be consciously devised and manufactured by man in the only examples of thought-transference over long distances at present discovered or laid bare to experiment and observation.

High and low Temperatures.—The past quarter of a century has witnessed a great development and application of the methods of producing both very low and very high temperatures. Sir James Dewar, by improved apparatus, has produced liquid hydrogen and a fall of temperature probably reaching to the absolute zero. A number of applications of extremely low temperatures to research in various directions has been rendered possible by the facility with which they may now be produced. Similarly high temperatures have been employed in continuation of the earlier work of Deville, and others by Moissan, the distinguished French chemist.

Progress in Chemistry.—In chemistry generally the theoretical tendency guiding a great deal of work has been the completion and verification of the "periodic law" of Mendeléeff; and on the other hand, the search by physical agents such as light and electricity for evidence as to the arrangement of atoms in the molecules of the most diverse chemical compounds. The study of "valency" and its outcome, stereo-chemistry, have been the special lines in which chemistry has advanced. As a matter of course hundreds, if not thousands, of new chemical bodies have been produced in the laboratory of greater or less theoretical interest. The discovery of the greatest practical and industrial importance in this connection is the production of indigo by synthetical processes, first by laboratory and then by factory methods, so as to compete successfully with the natural product. Von Baeyer and Heumann are the names associated with this remarkable achievement, which has necessarily dislocated a large industry which derived its raw material from British India.

(NOTE.—I had at first intended to give in this address a more detailed and technical statement of the progress of science than I have found possible when actually engaged in its preparation. The limits of time and space render any such survey on this occasion impossible, and moreover, the patience of even the general meeting of the British Association cannot be considered as unlimited. With a view to the preparation of a more detailed review, I had asked a number of friends and colleagues to send me notes on the progress and tendency in their own particular branches of science. They responded with the greatest generosity and unselfishness. I must entirely disclaim for them any responsibility for the brief detached statements made in the address. At the same time I should wish to thank them here by name for their most kind and timely help. They are Sir William Ramsay, Professor Soddy, Professor H. H. Turner, Professor Marr, Professor

Haddon, Dr. Smith Woodward, Professor Sherington, Professor Farmer, Professor Vines, Mr. D. Scott, Professor Meldola, Mr. Macdougall, Professor Poulton, Mr. C. V. Boys, Colonel MacMahon, and Professor Mackinder).

Astronomy.—A biologist may well refuse to offer any remarks on his own authority in regard to this earliest and grandest of all the sciences. I will therefore at once say that my friend the Savilian Professor of Astronomy in Oxford has turned my thoughts in the right direction in regard to this subject. There is no doubt that there has been an immense "revival" in astronomy since 1881; it has developed in every direction. The invention of the "dry plate," which has made it possible to apply photography freely in all astronomical work, is the chief cause of its great expansion. Photography was applied to astronomical work before 1881, but only with difficulty and haltingly. It was the dry-plate which made long exposures possible, and thus enabled astronomers to obtain regular records of faintly luminous objects such as nebulae and star-spectra. Roughly speaking, the number of stars visible to the naked eye may be stated as eight thousand; this is raised by the use of our best telescopes to a hundred million. But the number which can be photographed is indefinite and depends on length of exposure: a thousand million can certainly be so recorded.

The serious practical proposal to "chart the sky" by means of photography certainly dates from this side of 1881. The Paris Conference of 1887, which made an international scheme for sharing the sky among eighteen observatories (still busy with the work, and producing excellent results), originated with photographs of the comet of 1882, taken at the Cape Observatory.

Professor Pickering, of Harvard, did not join this co-operative scheme, but has gradually devised methods of charting the sky very rapidly, so that he has at Harvard records of the whole sky many times over, and when new objects are discovered he can trace their history *backwards* for more than a dozen years by reference to his plates. This is a wonderful new method, a mode of keeping record of present movements and changes which promises much for the future of astronomy. By the photographic method hundreds of new variable stars and other interesting objects have been discovered. New planets have been detected by the hundred. Up to 1881 two hundred and twenty were known. In 1881 only one was found; namely, Stephania, being No. 220, discovered on May 19. Now a score at least are discovered every year. Over five hundred are now known. One of these—Eros—(No. 433) is particularly interesting, since it is nearer to the sun than is Mars, and gives a splendid opportunity for fixing with increased accuracy the sun's distance from the earth. Two new satellites to Saturn and two to Jupiter have been discovered by photography (besides one to Jupiter in 1892 by the visual telescope of the Lick Observatory). One of the new satellites of Saturn goes round that planet the *wrong way*, thus calling for a fundamental revision of our ideas of the origin of the solar system.

The introduction of photography has made an immense difference in spectroscopic work. The spectra of the stars have been readily mapped out and classified, and now the motions in the line of sight of faint stars can be determined. This "motion in the line of sight," which was discernible but scarcely measurable with accuracy before, now provides one of the most refined methods in astronomy for ascertaining the dimensions and motions of the universe. It gives us velocities in miles per second instead of in an angular unit to be interpreted by a very imperfect knowledge of the star's distance. The method was in 1881 a mere curiosity, which Huggins was almost alone in having examined, though visual measures had been begun at Greenwich in 1875, and were continued for many years, only to be ultimately found to be affected by systematic error. The photographic method started by Vogel in 1887 really has made all the difference, and this work is now a vast department of astronomical industry. Among other by-products of the method are the "spectroscopic doubles,"

stars which we know to be double, and of which we can determine the period of revolution, though we cannot separate them visually by the greatest telescope.

Work on the sun has been entirely revolutionised by the use of photography. The last decade has seen the invention of the spectro-heliograph—which simply means that astronomers can now study *in detail* portions of the sun of which they could previously only get a bare indication.

More of the same story could be related, but enough has been said to show how full of life and progress is this most ancient and imposing of all sciences.

A minor though very important influence in the progress of astronomy has been the provision, by the expenditure of great wealth in America of great telescopes and equipments.

In 1877 my distinguished predecessor in the presidency of the British Association started a line of mathematical research which has been very fruitful and is of great future promise for astronomy. He was able himself last year to give some account of this research to the Association. On the present occasion I may mention that as recently as last April, at the Royal Astronomical Society, two important papers were read—one by Mr. Cowell and the other by Mr. Stratton—which have their roots in Sir George Darwin's work. The former was led to suggest that the day is lengthening ten times as rapidly as had been supposed, and the latter showed that in all probability the planets had all turned upside down since their birth.

And yet M. Brunetière and his friends wish us to believe that science is bankrupt and has no new things in store for humanity.

Geology.—In the field of geological research the main feature in the past twenty-five years has been the increasing acceptance of the evolutionary as contrasted with the uniformitarian view of geological phenomena. The great work of Suess, "Das Antlitz der Erde," is undoubtedly the most important contribution to physical geology within the period. The first volume appeared in 1885, and the impetus which it has given to the science may be judged of by the epithet applied to the views for which Suess is responsible—"the New Geology." Suess attempts to trace the orderly sequence of the principal changes in the earth's crust since it first began to form. He strongly opposes the whole theory of elevation, and accounts for the movements as due to differential collapse of the crust, accompanied by folding due to tangential stress. Among special results gained by geologists in the period we survey may be cited new views as to the origin of the crystalline schists, favouring a return to something like the hypogene origin advocated by Lyell; the facts as to deep-sea deposits, now in course of formation, embodied in the "Challenger" reports on that subject; the increasing discrimination and tracking of those minor divisions of strata called "zones"; the assignment of the Olennellus fauna of Cambrian age to a position earlier than that of the Paradoxides fauna; the discovery of Radiolaria in palaeozoic rocks by special methods of examination, and the recognition of Graptolites as indices of geological horizons in lower palaeozoic beds. Glacially eroded rocks in boulder-clays of permo-carboniferous age have been recognised in many parts of the world (e.g. Australia and South Africa), and thus the view put forward by W. T. Blanford as to the occurrence of the same phenomena in conglomerates of this age to India is confirmed. Eozoon is finally abandoned as owing its structure to an organism. The oldest fossiliferous beds known to us are still far from the beginning of life. They contain a highly developed and varied animal fauna—and something like the whole of the older moiety of rocks of aqueous origin have failed as yet to present us with any remains of the animals or plants which must have inhabited the seas which deposited them. The boring of a coral reef initiated by Professor Sollas at the Nottingham meeting of this Association in 1893 was successfully carried out, and a depth of 1114½ feet reached. Information of great value to geologists was thus obtained.

Animal and Vegetable Morphography.—Were I to attempt to give an account of the new kinds of animals and plants discovered since 1881, I should have to read out a bare catalogue, for time would not allow me to explain the interest attaching to each. Explorers have been busy in all parts of the world—in Central Africa, in the Antarctic, in remote parts of China, in Patagonia and Australia, and on the floor of the ocean, as well as in caverns, on mountain tops, and in great lakes and rivers. We have learnt much that is new as to distribution; countless new forms have been discovered, and careful anatomical and microscopical study conducted on specimens sent home to our laboratories. I cannot refrain from calling to mind the discovery of the eggs of the Australian duckmole and hedgehog; the fresh-water jelly-fish of Regent's Park, the African lakes, and the Delaware River; the marsupial mole of Central Australia; the okapi; the young and adult of the mud-fishes of Australia, Africa, and South America; the fishes of the Nile and Congo; the gill-bearing earth worms and mud worms; the various forms of the caterpillar-like *Peripatus*; strange deep-sea fishes, polyps and sponges.

The main result of a good deal of such investigation is measured by our increased knowledge of the pedigree of organisms, what used to be called "classification." The anatomical study by the Australian professors, Hill and Wilson, of the teeth and the fetus of the Australian group of pouched mammals—the marsupials—has entirely upset previous notions, to the effect that these were a primitive group, and has shown that their possession of only one replacing tooth is a retention of one out of many such teeth (the germs of which are present), as in placental mammals; and further that many of these marsupials have the nourishing outgrowth of the fetus called the placenta fairly well developed, so that they must be regarded as a degenerate side-branch of the placental mammals, and not as primitive forerunners of that dominant series.

Speculations as to the ancestral connection of the great group of vertebrates with other great groups have been varied and ingenious; but most naturalists are now inclined to the view that it is a mistake to assume any such connection in the case of vertebrates of a more definite character than we admit in the case of starfishes, shellfish, and insects. All these groups are ultimately connected by very simple, remote, and not by proximate ancestors, with one another and with the ancestors of vertebrates.

The origin of the limbs of vertebrates is now generally agreed to be correctly indicated in the Thatcher-Mivart-Balfour theory to the effect that they are derived from a pair of continuous lateral fins, in fish-like ancestors, similar in every way to the continuous median dorsal fin of fishes.

The discovery of the formation of true spermatozoa by simple unicellular animals of the group Protozoa is a startling thing, for it had always been supposed that these peculiar reproductive elements were only formed by multicellular organisms. They have been discovered in some of the gregarina-like animalcules, the Coccidia, and also in the blood-parasites.

Among plants, one of the most important discoveries relates to these same reproductive elements, the spermatozoa, which by botanists are called antherozoids. A great difference between the whole higher series of plants, the flowering plants or phanerogams, and the cryptogams or lower plants, including ferns, mosses, and algae, was held to be that the latter produce vibratile spermatozoa like those of animals which swim in liquid and fertilise the motionless egg-cell of the plant. Two Japanese botanists (and the origin of this discovery from Japan, from the University of Tokio, in itself marks an era in the history of science), Hirase and Ikeno, astonished the botanical world fifteen years ago by showing that motile antherozoids or spermatozoa are produced by two gymnosperms, the gingko tree (or *Salisburya*) and the

cycads. The pollen tube, which is the fertilising agent in all other phanerogams, develops in these cone-bearing trees beautiful motile spermatozoa, which swim in a cup of liquid provided for them in connection with the ovules. Thus a great distinction between phanerogams and cryptogams was broken down, and the actual nature of the pollen-tube as a potential parent of spermatozoids demonstrated.

When we come to the results of the digging out and study of extinct plants and animals, the most remarkable results of all in regard to the affinities and pedigree of organisms have been obtained. Among plants the transition between cryptogams and phanerogams has been practically bridged over by the discovery that certain fern-like plants of the Coal Measures—the Cycadofilices, supposed to be true ferns, are really seed-bearing plants and not ferns at all, but phanerogams of a primitive type, allied to the cycads and gymnosperms. They have been rechristened Pteridosperms by Scott, who, together with F. Oliver and Seward, has been the chief discoverer in this most interesting field.

By their fossil remains whole series of new genera of extinct mammals have been traced through the tertiary strata of North America and their genetic connections established; and from yet older strata of the same prolific source we have almost complete knowledge of several genera of huge extinct Dinosaurs of great variety of form and habit.

The discoveries by Seeley at the Cape, and by Amalitzky in North Russia of identical genera of Triassic reptiles, which in many respects resemble the Mammalia and constitute the group Theromorpha, is also a prominent feature in the palæontology of the past twenty-five years. Nor must we forget the extraordinary Silurian fishes discovered and described in Scotland by Professor Traquair. The most important discovery of the kind of late years has been that of the Upper Eocene and Miocene Mammals of the Egyptian Fayum, excavated by the Egyptian Geological Survey, and by Dr. Andrews, of the Natural History Museum, who has described and figured the remains. They include a huge four-horned animal as big as a rhinoceros, but quite peculiar in its characters—the *Arisinotherium*—and the ancestors of the elephants, a group which was abundant in Miocene and Pliocene times in Europe, and Asia, and in still later times in America, and survives at the present day in its representatives the African and Indian elephant. One of the European extinct elephants—the *Tetrabelodon*—had, we have long known, an immensely long lower jaw with large chisel-shaped terminal teeth. It had been suggested by me that the modern elephant's trunk must have been derived from the soft upper jaw and nasal area, which rested on this elongated lower jaw, by the shortening (in the course of natural selection and modification by descent) of this long lower jaw, to the present small dimensions of the elephant's lower jaw, and the consequent down-dropping of the unshortened upper jaw and lips, which thus become the proboscis. Dr. Andrews has described from Egypt and placed in the Museum in London specimens of two new genera—one *Palæomastodon*, in which there is a long powerful jaw, an elongated face, and an increased number of molar teeth; the second, *Meritherium*, an animal with a hippopotamus-like head, comparatively minute tusks, and a well-developed complement of incisor, canine, and molar teeth, like a typical ungulate mammal. Undoubtedly we have in these two forms the indications of the steps by which the elephants have been evolved from ordinary-looking pig-like creatures of moderate size, devoid of trunk or tusks. Other remains belonging to this great mid-African Eocene fauna indicate that not only the Elephants but the Sirenia took their origin in this area. Amongst them are also gigantic forms of Hyrax, like the little Syrian coney and many other new mammals and reptiles.

Another great area of exploration and source of new

things has been the southern part of Argentina and Patagonia, where Ameghino, Moreno, and Scott, of Princeton, have brought to light a wonderful series of extinct ant-eaters, armadillos, huge sloths, and strange ungulates, reaching back into early Tertiary times. But most remarkable has been the discovery in this area of remains which indicate a former connection with the Australian land surface. This connection is suggested by the discovery in the Santa Cruz strata, considered to be of early Tertiary date, of remains of a huge horned tortoise which is generically identical with one found fossil in the Australian area of later date, and known as *Miolania*. In the same wonderful area we have the discovery in a cave of the fresh bones, hairy skin, and dung of animals supposed to be extinct, viz., the giant sloth, *Mylodon*, and the peculiar horse, *Onohippidium*. These remains seem to belong to survivors from the last submergence of this strangely mobile land-surface, and it is not improbable that some individuals of this "extinct" fauna are still living in Patagonia. The region is still unexplored, and those who set out to examine it have, by some strange fatality, hitherto failed to carry out the professed purpose of their expeditions.

I cannot quit this immense field of gathered fact and growing generalisation without alluding to the study of animal embryology and the germ-layer theory, which has to some extent been superseded by the study of embryonic cell-lineage, so well pursued by some American microscopists. The great generalisation of the study of the germ-layers and their formation seems to be now firmly established—namely, that the earliest multicellular animals were possessed of one structural cavity, the enteron, surrounded by a double layer of cells, the ectoderm and endoderm. These Enterocœla or Cœlentera gave rise to forms having a second great body cavity, the cœlom, which originated not as a split between the two layers, as was supposed twenty-five years ago by Haeckel and Gegenbaur and their pupils, but by a pouching of the enteron to form one or more cavities in which the reproductive cells should develop—pouchings which became nipped off from the cavity of their origin, and formed thus the independent cœlom. The animals so provided are the Cœlomocœla (as opposed to the Enterocœla), and comprise all animals above the polyps, jelly-fish, corals, and sea-anemones. It has been established in these twenty-five years that the cœlom is a definite structural unit of the higher groups, and that outgrowths from it to the exterior (cœlomoducts) form the genital passages, and may become renal excretory organs also. The vascular system has not, as it was formerly supposed to have, any connection of origin with the cœlom, but is independent of it, in origin and development, as also are the primitive and superficial renal tubes known as nephridia. These general statements seem to me to cover the most important advance in the general morphology of animals which we owe to embryological research in the past quarter of a century. (See the Introduction to Part II. of "A Treatise on Zoology," edited by E. Ray Lankester; London, A. and C. Black).

Before leaving the subject of animal morphology I must apologise for my inability to give space and time to a consideration of the growing and important science of anthropology, which ranges from the history of human institutions and language to the earliest prehistoric bones and implements. Let me therefore note here the discovery of the cranial dome of *Pithecanthropus* in a river gravel in Java—undoubtedly the most ape-like of human remains, and of great age; and, further, the Eoliths of Prestwich, in the human authorship of which I am inclined to believe, though I should be sorry to say the same of all the broken flints to which the name "Eolith" has been applied. The systematic investigation and record of savage races have taken on a new and scientific character. Such work as Baldwin Spencer's and Haddon's in Australasia furnish examples of what is being done in this way.

To be continued).

THE COAL-TAR COLOUR JUBILEE.

IN connection with the Perkin Jubilee, celebrated last week, a correspondent has drawn our attention to the following extract, written by J. C. Brough, which appeared in *Fun* fifty years ago. At this holiday season, when laboratory work is becoming temporarily less strenuous, we make no apology for presenting it to our readers.

COMIC CHEMICALS. (From *Fun*).

IN the July number of the *Chemical Society's Journal* there is an essay (Paper read June 15, 1856) "On the Action of Nascent Hydrogen on Azodinaphthylidiamine"—a subject which is hardly likely to rivet the attention of non-professional readers, especially as it is dealt with in prose. Treated metrically, perhaps, it might appeal to a wider circle; in this conviction we have thrown the treatise into melodious verse, confining ourselves, as much as possible, to words of less than ten syllables. We dedicate our lyric to Mr. W. H. Perkin, the author of the original essay in the *C. S. J.*; and we call it, from circumstances under which it was composed—

AN ALCOHOLIC SOLUTION. (*Air*: "Guy Fawkes").

The many metamorphoses which bodies undergo, sirs,
When subjected to hydrogen, all chemists ought to know,
sirs;

But only one who occupies the proud position I am in
Can calculate its action on Azodinaphthylidiamine.

Bow, wow, wow, &c.

That hydrogen, in such a case, is certain to decolorize,
Can hardly be a question for a man who has a skull or
eyes.

Solutions alcoholic must be saturated clammily
In nipperkins or pippetkins (you know the Perkin family).

Bow, wow, wow, &c.

You turn it to a palish buff, supposing you begin, sirs,
By carefully digesting it with granulated tin, sirs;
Then borrow some decanters, just to bottle the solution up;
But don't attempt to drink it, or you'll knock your consti-
tution up.

Bow, wow, wow, &c.

With sulphuretted hydrogen the residue is treated;
For my part, it's a sort of treat I should not want repeated.
Then filter pretty quickly—if you filter *slow*, 't will militate
Against the operation it may otherwise facilitate.

Bow, wow, wow, &c.

The residue looks dirty, and of course you'll say, "I'm
sure if I'd

A little boiling water, I should like to get it purified."
Add hydrochloric acid—it will be of use in hurrying
The crystallising process, and will save a deal of worrying.

Bow, wow, wow, &c.

But no! If we were to go on at this rate, the next number of *Fun* would have to appear in three large volumes; and perhaps the Editor would n't like to be thought eccentric. However, if any respectable chemist and druggist is dying to learn what the action of nascent hydrogen on azodinaphthylidiamine may be, let him send a stamped envelope and a dozen boxes of his best ipecacuanha lozenges to 80 Fleet Street, and the envelope shall be returned without loss of time.

Influence of Substituents on the Tint of Malachite Green.—E. Noelting and P. Gerlinger.—The effects of nitro and hydroxyl groups upon the colour of malachite green have been investigated by others, and the authors have now determined the corresponding effects of the methoxyl group, chlorine derivatives, and sulpho-derivatives. The first of these in the ortho-position renders the colour more blue, in the para more yellow, and has no effect when in the meta position. The halogen produces a more decided blue tint in the ortho-position than the nitro group.

—*Berichte*, xxxix., No. 9.

NOTES OF A COURSE OF LECTURES ON THE
OLD AND NEW CHEMISTRY.†

II. EXTRACTS FROM DIFFERENT AUTHORS RELATING TO
THE NEW CHEMISTRY.

By Prof. Sir JAMES DEWAR, F.R.S., &c.

(Continued from p. 40).

*Faraday's Discovery of Electro-chemical Decomposition.—
Tyndall.*

"His paper on electro-chemical decomposition, received by the Royal Society on January 9, 1834, opens up with the proposal of a new terminology. He would avoid the word 'current' if he could. He does abandon the word 'poles' as applied to the ends of a decomposing cell, because it suggests the idea of attraction, substituting for it the perfectly neutral term Electrodes. He applied the term Electrolyte to every substance which can be decomposed by the current, and the act of decomposition he called Electrolysis. All these terms have become current in science. He called the positive electrode the Anode, and the negative one the Cathode, but these terms, though frequently used, have not enjoyed the same currency as the others. The terms Anion and Cation, which he applied to the constituents of the decomposed electrolyte, and the term Ion, which included both anions and cations, are still less frequently employed.

"Faraday now passes from terminology to research; he sees the necessity of quantitative determinations, and seeks to supply himself with a measure of voltaic electricity. This he finds in the quantity of water decomposed by the current. He tests this measure in all possible ways to assure himself that no error can arise from its employment.

"Sending the same current through a series of cells containing mixtures of sulphuric acid and water of different strengths, he finds, however the proportion of acid to water might vary, the same amount of gas to be collected in all the cells. A crowd of facts of this character forced upon Faraday's mind the conclusion that the amount of electro-chemical decomposition depends, not upon the size of the electrodes, not upon the intensity of the current, not upon the strength of the solution, but solely upon the quantity of electricity which passes through the cell. The quantity of electricity he concludes is proportional to the amount of chemical action. On this law Faraday based the construction of his celebrated Voltameter, or Measurer of Voltaic electricity.

"With the indications of his voltameter he compared the decomposition of other substances both singly and in series. He submitted his conclusions to numberless tests. He purposely introduced secondary actions. He endeavoured to hamper the fulfilment of those laws which it was the intense desire of his mind to see established. But from all these difficulties emerged the golden truth, that under every variety of circumstances the decompositions of the voltaic current are as definite in their character as those chemical combinations which gave birth to the atomic theory. This law of electro-chemical decomposition ranks, in point of importance, with that of definite combining proportions in chemistry."

Chemistry and New Elements.—Herschel.

"It is, of all the sciences, perhaps, the most completely an experimental one; and even its theories are, for the most part, of that generally intelligible and readily applicable kind, which demand no intense concentration of thought, and lead to no profound mathematical researches. The simple process of inductive generalisation, grounded on the examination of numerous facts, all of them presenting considerable intrinsic interest, has sufficed, in most instances, to lead, by a clear and direct road, to its highest laws yet known. But, on the other hand, these laws, when stated, are not yet fully sufficient to lead us,

except in very limited cases, to a deductive knowledge of particulars never before examined, at least, not without great caution, and constant appeal to experiment as a check on our reasoning; so that we are justified in regarding the axioms of chemistry, the true handles of deductive reasoning, as still unknown, and, perhaps, likely long to remain so. This is no fault of its cultivators, who have comprised in their list the highest and most varied talents and industry, but of the inherent complexity of the subject, and the infinite multitude of causes which are concerned in the production of every, even the simplest, chemical phenomenon.

"And first, then, with reference to the discovery of new elements, it will be observed, that philosophical chemistry no more aims at determining the one essential element out of which all matter is framed—the one ultimate principle of the universe—than astronomy at discovering the origin of the planetary movements in the application of a determinate projectile force in a determinate direction, or geology at ascending to the creation of the earth. There may be such an element. Some singular relations which have been pointed out in the atomic weights of bodies seem to suggest to minds fond of speculation that there is; but philosophical chemistry is content to wait for some striking fact, which may either occur unexpectedly or be led to by the slow progress of enlarged views, to disclose to us its existence. Still, the multiplication of so-considered elementary bodies has been considered by some as an inconvenience. We confess we do not coincide with this view. Whatever they be, the obstinacy with which they resist decomposition shows that they are ingredients of a very high and primary importance in the economy of nature; and such as, in any state of science, it would be indispensably necessary to be perfectly familiar with. Like particular theorems in geometry, which, though not rising to the highest point of generality, have yet their several scopes and ranges of extensive application, they must be well and perfectly understood in all their bearings. Should we ever arrive at an analysis of these bodies, the chemical properties of the new elements which will then come into view will be known only by our knowledge of these, or of other compounds of the same class, which they may be capable of forming. Not but that such an analysis would be a most important, and indeed triumphant achievement, and change the face of chemistry; but it would undo nothing that has been done, and render useless no point of knowledge which we have yet arrived at."

*Principal Features in the Progress of the New Chemistry
to the Year 1833.—Sir John Herschel.*

1. The discovery of the proximate, if not the ultimate, elements of all bodies, and the enlargement of the list of known elements to its present extent of between fifty and sixty substances.
2. The development of the doctrine of latent heat by Black, with its train of important consequences, including the scientific theory of the steam engine.
3. The establishment of Wenzel's law of definite proportions on his own experiments, and those of Richter, a discovery subsequently merged in the greater generality of the atomic theory of Dalton.
4. The precise determination of the atomic weights of the different chemical elements, mainly due to the astonishing industry of Berzelius and his unrivalled command of chemical resources, as well as to the researches of the other chemists of the Swedish and German School, and of our countryman, Dr. Thomson.
5. The assimilation of gases and vapours, by which we are led to regard the former, universally as particular cases of the latter, a generalisation resulting chiefly from the experiments of Faraday on the condensation of the gases, and those of Gay-Lussac and Dalton, on the laws of their expansion by heat compared with that of vapours.
6. The establishment of the laws of the combination of gases and vapours by definite volumes, by Gay-Lussac.
7. The discovery of the chemical effects of electricity

* Delivered at the Royal Institution, May 26th, 1906.

and the decomposing agency of the Voltaic pile by Nicholson and Carlisle; the investigation of the laws of such decompositions, by Berzelius and Hisinger; the decomposition of the alkalis, by Davy; and the consequent introduction into chemistry of new and powerful agents in their metallic bases.

8. The application of chemical analysis to all the objects of organised or unorganised nature, and the discovery of the ultimate constituents of all, and the proximate ones of organic matter, and the recognisance of the important distinctions which appear to divide these great classes of bodies from each other.

9. The applications of chemistry to innumerable processes in the arts, and among other useful purposes to the discovery of the essential medical principles in vegetables, and to important medicaments in the mineral kingdom.

10. The establishment of the intimate connection between chemical composition and crystalline form, by Haüy and Vauquelin, with the successive rectifications the statement of that connection has undergone in the hands of Mitscherlich, Rose, and others, with the progress of chemical crystallographical knowledge.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, July 5th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

(Concluded from p. 45).

141. "The Alkylation of Rhamnose." By THOMAS PURDIE and CHARLES ROBERT YOUNG.

By complete methylation with silver oxide and methyl iodide, acetone- and methyl-rhamnosides yield respectively dimethyl acetonerhamnoside and trimethyl methyl-rhamnoside, and by hydrolysing these compounds di- and tri-methylrhamnose respectively are obtained. The rhamnose derivatives described are liquids, but, all of them excepting dimethyl rhamnose being volatile without decomposition, it was possible to isolate them by fractional distillation under reduced pressure.

Dimethyl- and trimethyl-rhamnose give crystalline phenylhydrazones, and display the ordinary properties of reducing sugars. Trimethyl rhamnose is re-converted into trimethyl methylrhamnoside by condensation with methyl alcohol and also by the silver oxide method of alkylation; the former process gives mainly the α -form of the aldose, the latter a mixture composed largely of the β -form. The presence of the β -isomeride was recognised not only by its rotatory power, but also by the rapidity of its hydrolysis. The rotatory powers of the substances described fall into line with those of glucose and its corresponding derivatives.

142. "The Alkylation of l-Arabinose." By THOMAS PURDIE and ROBERT EVSTAFIEFF ROSE.

By methylating Fischer's α -methylarabinoside with silver oxide and methyl iodide, trimethyl- α -methylarabinoside is obtained in large well-formed crystals (m. p. 43–45°), and by hydrolysing this with dilute hydrochloric acid trimethyl arabinose is produced. This substance is a liquid (b. p. 148–152°, 19 m.m.), but otherwise it exhibits the usual properties of a reducing sugar. It can be methylated by condensation with methyl alcohol, and also by treatment with methyl iodide and silver oxide, the product in both cases being a mixture of the isomeric trimethyl methylarabinosides. The condensation process yields the crystalline ϵ -isomeride in large proportion, the silver oxide process mainly the β -isomeride. The latter substance is apparently a liquid, and it could not be isolated, but its presence in the mixture was recognised by its undergoing hydrolysis more rapidly than the isomeric α -form.

In preparing Fischer's α -methylarabinoside, a small

quantity of the β -methylarabinoside was obtained in crystalline prisms melting at 115–117°.

With respect to rotatory power, the isomeric methylarabinosides and trimethyl methylarabinosides show relations similar to those of the corresponding derivatives of d-glucose.

143. "The Esters of Triacetic Lactone and Triacetic Acid." By FOSTER SPROXTON.

Ethyl triacetate, $\text{Me} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, is formed by heating triacetic lactone with dry alcohol in sealed tubes, and may be obtained pure by decomposing its copper salt with sulphuretted hydrogen. It gives a deep red coloration with ferric chloride.

The ethyl and methyl salts of triacetic lactone have been prepared by the action of ethyl and methyl iodides on the silver salt of the lactone. The ethyl ester could not be obtained in the pure condition. Like the analogous esters of dehydracetic acid, they have an acid reaction in aqueous solution. This property has been shown to be due, in both the triacetic lactone and dehydracetic acid derivatives, to partial hydrolysis of the esters by water. Complete hydrolysis takes place on boiling, and the parent lactone can be recovered from the solution.

144. "Optically Active Reduced Naphthoic Acids. Part II. The Resolution of the Tetrahydronaphthoic Acids." By ROBERT HOWSON PICKARD and JOSEPH YATES.

1:2:3:4-Tetrahydro-1-naphthoic acid and 1:2:3:4-tetrahydro-2-naphthoic acid have each been resolved into their optical antipodes by the fractional crystallisation from acetone of the l-menthylamine salts.

The laevo-isomeride of the first has $[\text{M}]_D - 28.1^\circ$ in chloroform and -92.1° in benzene, that of the second having $[\text{M}]_D + 91.2^\circ$ in chloroform and $+87.9^\circ$ in benzene. The sodium salts when dissolved in water have respectively $[\text{M}]_D - 21.1^\circ$ and -90.5° .

145. "The Velocity of Chemical Change in the Polymethylene Series." By N. MENSCHUTKIN, sen.

The general results of the study of the velocity of chemical change in polymethylene derivatives are as follows:—

1. The formation of the closed polymethylene chain from an open saturated chain of normal structure proceeds with increase of velocity. The maximum increase occurs in the formation of the pentamethylene ring; in the case of the hexamethylene ring the increase is less, and the heptamethylene ring is formed with the minimum increase of velocity.

2. The increase of velocity at the closing of the open chain is not a specific property of the polymethylene ring, but is a general phenomenon observed in the formation of all closed chains, alicyclic and heterocyclic.

3. The constants of velocity decrease according as the number of methylene groups in the polymethylene rings increases. The decrease is of the same order as is observed in the homologous series of open chain saturated carbon compounds of normal structure.

4. The secondary polymethylene alcohols, in which the hydroxyl group is attached to the carbon atom of the ring, are typical secondary alcohols. Their esterification constants are higher than those of the saturated secondary alcohols of normal structure. Hence, the polymethylene alcohols give higher constants than all of the secondary alcohols studied. The constants of the derivatives of cyclopentanol are the highest; cyclohexanol gives much lower values, and cycloheptanol still less.

5. The side chain combined with the carbon atom united with the hydroxyl group gives rise to the formation of the polymethylene tertiary alcohols. Their esterification constants are low, but esterification proceeds regularly; this is not the case with saturated tertiary alcohols, but is characteristic of phenols.

6. When the side chains are in the ortho- and diorthopositions, a great decrease in the esterification constants is observed. This effect, commonly ascribed to the benzene ring alone, is a general property of all classes of chains

whether open or closed, and containing carbon or other elements.

7. When the side chain is in the position 3 or 4 of the polymethylene ring, an increase of esterification constants is observed, so much so that in the hexamethylene series the value of the constant of the first member of the series is exceeded.

8. This property is not confined to the polymethylene ring, but applies generally to ringed systems, alicyclic and heterocyclic. As open chain compounds show no such increase of velocity, this is an important character of the closed chains.

9. When a hexamethylene ring is introduced into the open chain of an alcohol, the decrease of the esterification constant is much more than is effected by the benzene ring.

10. Hexamethylene, like hexane, exerts a very considerable retarding influence when used as a solvent in these reactions.

146. "Hydrolysis of Ammonium Salts by Water." By ERNEST GEORGE HILL.

The author aspirated a measured volume of air through solutions of different ammonium salts, the strengths of the solutions being normal, fifth-normal, and twenty-fifth-normal. The ammonia passing over was absorbed in water, or, when the amount was large, in acid. In the first case, the ammonia was estimated from the conductivity of the solution; in the latter case, by titration. It was found that for strong acids the equation—

$$\frac{C \text{ Acid} \times C \text{ Base}}{C \text{ Salt}} = K,$$

and for weak acids—

$$\frac{C \text{ Acid} \times C \text{ Base}}{C^2 \text{ Salt}} = K$$

holds good for the concentrations of salt used.

The constants obtained in the case of the salts of monobasic acids are inversely proportional to the molecular conductivities of the acids, and agree well with the values obtained for the strength of the acids by the various dynamical methods. In the case of dibasic acids, the constants are irregular. It is shown that the constant must depend on both the first and second ionisation-coefficients of the acids.

The author described the method employed for estimating ammonia by taking the resistance of its solution in conductivity water and comparing this with the resistance curve of ammonia. The method gave good results with solutions containing from 0.00027 to 0.009 per cent.

147. "The Addition of Alkyl Halides to Alkylated Sugars and Glucosides." By JAMES COLQUHOUN IRVINE and AGNES MARION MOODIE.

When solutions of the equilibrium mixture of tetramethyl glucose in ordinary organic solvents are cooled from +20° to -20°, the specific rotations undergo very little alteration, and, on re-heating to the initial temperature, the values originally found for the rotatory powers are exactly duplicated. When, however, an alkyl halide is used as solvent, the specific rotation at first increases slightly with fall of temperature and then rapidly diminishes on further cooling. On re-heating the cooled solution to 20°, distinct downward multi-rotation was observed before the initial value was reached. The same regularities were shown by solutions of molecular proportions of the sugar and alkyl halides or hydrogen chloride in carbon tetrachloride.

The results point to the formation, during cooling, of oxonium compounds of the sugar with alkyl halides, and the α -form of the aldose appears to be more reactive than the β -isomeride. This was shown by a cycle of changes in specific rotation observed in the case of a solution in isopropyl iodide which had been cooled from 20° to 0°:— (a) Rapid decrease at 0°, due to oxonium formation; (b) subsequent upward multi-rotation at 0°, owing to the partial conversion, $\beta \rightarrow \alpha$, in the uncombined sugar; (c) on re-heating to 20°, owing to dissociation of the oxonium compound, a rapid increase at constant temperature took

place, followed by (d) downward multi-rotation at 20° to the initial value.

Tetramethyl α -methylglucoside also behaves abnormally when cooled in ethyl iodide solution, but the β -isomeride gives no indication of addition of the solvent. Comparable results were obtained with tetramethyl mannose and tetramethyl α -methylmannoside, but non-alkylated sugars or glucosides, when examined in mixtures of methyl alcohol and alkyl iodides, gave negative results.

The following notes have been received since the meeting:—

148. "Note on the Preparation of Ethyl Acetonedicarboxylate." By ERNEST ORMEROD.

In attempting to prepare ethyl acetonedicarboxylate, on fractionating the crude ester prepared by the method described by v. Pechmann (*Annalen*, 1891, cclxi., 160) under reduced pressure, only a small quantity of volatile material was obtained, which on examination proved to be principally acetoacetic ester. The main product, which on cooling solidified to a white crystalline mass, was ethylorcintricarboxylate.

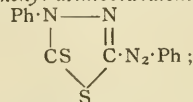
Wolfman and v. Pechmann (*Ber.*, 1898, xxxi., 2014) have shown that ethylorcintricarboxylate is formed if an alcoholic solution of acetonedicarboxylic acid saturated with hydrogen chloride is allowed to stand for two or three weeks, and it was at first thought possible that the condensation had been brought about in this way during the preparation, but on examination it was found that the crude ester contained only a very small quantity of the orcinol derivative. It appeared very strange that the condensation should take place so readily, as according to Jerdan (*Trans.*, 1899, lxxiii., 808) the pure ester may be heated at 180° for a considerable time without any condensation taking place. Finally, it was found that the condensation was brought about by the presence of a small quantity of calcium chloride which had been dissolved by the alcohol-etheral solution of the ester. This view was shown to be correct by the fact that if the pure ester be heated with a trace of calcium chloride at 180° for a short time, the amount of orcinol derivative formed corresponds to 4 per cent of the theoretical. If the ethereal solution of the crude ester is dried over fused sodium sulphate, it may be distilled under reduced pressure without any condensation taking place.

During an attempt to prepare pure methyl acetonedicarboxylate, Dootson (*Trans.*, 1900, lxxiv., 1196) obtained a crude product which, on distillation under reduced pressure, condensed very readily to form methyl orcintricarboxylate, and he came to the conclusion that the methyl ester cannot be distilled without this condensation taking place. It seems improbable that the methyl ester should differ in this respect from the ethyl ester, and, although Dootson does not state how the ethereal solution was dried, it is probable that the crude ester contained some inorganic substance which promoted the condensation.

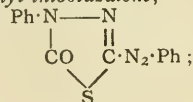
149. "The Interaction of Nitroformazyl, Carbon Bisulphide, and Potassium Hydroxide. A Contribution to the Chemistry of the Thiobiazalones and the Xanthates." By ERNEST ORMEROD.

The peculiar position of the nitro-group in nitroformazyl confers on this compound very abnormal properties; thus, by the interaction of nitroformazyl, carbon bisulphide, and potassium hydroxide, three compounds are obtained:—

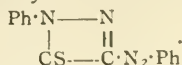
1-Phenyl-3-azophenyl-dithiobiazalone,—



1-phenyl-3-azophenyl thiobiazalone,—



and 1-phenyl-3-azophenyl-2-thioazethane,—



The three compounds are formed in varying quantities, depending on the solvent used and the conditions under which the experiment is carried out. Using alcohol as solvent, at the ordinary temperature the monothioibiazalone is almost exclusively formed, whilst if the interaction takes place at higher temperatures all three compounds are produced simultaneously; on using acetone or carbon bisulphide as the solvent, only the dithioibiazalone is formed.

The results obtained are interesting, as proving that a boiling alcoholic solution of carbon bisulphide and potassium hydroxide contains potassium xanthate, potassium dithiocarbonate, and potassium trithiocarbonate.

The author finds that the nitroformazyl is first reduced to formazylmercaptan, which is then acted on by the potassium xanthate, forming the dithioibiazalone, and by the potassium dithiocarbonate, forming the monothioibiazalone. The thioazethane is apparently produced by the interaction of the potassium trithiocarbonate and the nitroformazyl.

The constitution of the biazalones obtained was proved by an examination of their decomposition products and by synthesis; the dithioibiazalone was synthesised from formazylmercaptan and thiophosgene, and the monothioibiazalone from formazylmercaptan and phosgene.

150. "Aldehydrol and the Hydrates of Compounds containing a Carbonyl Group." By WILLIAM MORRIS COLLES. Concentrated aqueous solutions of aldehyde, acetone, formic, acetic, monochloroacetic, and trichloroacetic acids were cooled to low temperatures in an apparatus fitted with a combined filtering and stirring tube. The solutions, made up quantitatively in definite molecular proportions, were contained in a long stoppered weighing tube into which the combined filtering and stirring tube fitted. This in turn was clamped inside a large vacuum vessel containing absolute alcohol, which, when cooled by liquid air, constituted the freezing mixture. Cooling was brought about very gradually, and the solutions were very rapidly stirred. Several crystalline hydrates were obtained, the mother-liquor being separated as soon as crystallisation had occurred. The following compounds of special interest were obtained:—Aldehydrol, $\text{CH}_3\text{CH}(\text{OH})_2$, at -90° , a hydrol of formic acid, possibly *ortho*-formic acid, $\text{HC}(\text{OH})_3$; *ortho*-acetic acid, $\text{CH}_3\text{C}(\text{OH})_3$; and *ortho*-monochloroacetic acid, $\text{CH}_2\text{ClC}(\text{OH})_3$. The analyses of the last two compounds, owing to experimental difficulties, were not very close. Acetone gave no result, and with trichloroacetic acid a hydrate containing 3 mols. of water was obtained. The hydrates of formic acid were fairly thoroughly investigated, and the following were obtained in a fairly pure crystalline condition:— $\text{CH}_2\text{O}_2, 4\text{H}_2\text{O}$, $4\text{CH}_2\text{O}_2, 7\text{H}_2\text{O}$, $4\text{CH}_2\text{O}_2, 3\text{H}_2\text{O}$, $3\text{CH}_2\text{O}_2, 2\text{H}_2\text{O}$.

UNIVERSITY OF DURHAM.

ARMSTRONG COLLEGE, Newcastle-upon-Tyne.

Principal—Sir ISAMBARD OWEN, D.C.L., M.D.

SESSION OF 1906-7.

MATRICULATION and EXHIBITION EXAMINATIONS, SEPTEMBER 24-29th.

OPENING OF TERM, OCTOBER 2nd.

Particulars of Curricula for University Degrees and College Diplomas in ENGINEERING, ELECTRICAL ENGINEERING, NAVAL ARCHITECTURE, MINING, METALLURGY, AGRICULTURE, PURE SCIENCE, and LETTERS, as well as of Fellowships, Scholarships, and Exhibitions, and of facilities for residence, on application to—

F. H. PRUEN, Secretary,
Armstrong College, Newcastle-upon-Tyne.

UNIVERSITY OF MANCHESTER.

CHEMISTRY COURSE.

A Prospectus, containing full particulars of the Lecture and Laboratory Courses in INORGANIC and ORGANIC CHEMISTRY, qualifying for the DEGREES IN CHEMISTRY and for the CERTIFICATE IN APPLIED CHEMISTRY, will be forwarded on application to the REGISTRAR.

UNIVERSITY OF GLASGOW.

The MEDICAL SESSION will be opened on THURSDAY, OCTOBER 18, 1906. A Syllabus containing full particulars as to the Course of Education and as to the Preliminary Examination required to be passed by Students before beginning Medical study, may be obtained by applying to Mr. W. INNES ADDISON, Assistant Clerk.

UNIVERSITY OF BIRMINGHAM.

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The Session 1906-7 commences October 1st, 1906.

ALL COURSES AND DEGREES ARE OPEN TO BOTH MEN AND WOMEN STUDENTS.

In the Medical School there is a separate Dissecting Room for Women, with a qualified Woman Demonstrator.

Graduates, or persons who have passed Degree Examinations of other Universities, may, after two years' study or research, take a Master's Degree.

SYLLABUSES with full information as to Lecture and Laboratory Courses, Regulations for Degrees, Diplomas, &c., Exhibitions and Scholarships, will be sent on application to the Secretary of the University.

EGYPTIAN GOVERNMENT.

MINISTRY OF EDUCATION.

The following post at the School of Medicine, CAIRO, is vacant:—

ASSISTANT TO THE PROFESSOR OF CHEMISTRY.

The appointment is for two years, and may be renewed at the end of that time. Applicants should forward copies of testimonials, and such other particulars as are mentioned below.

The pay of the Post is £320 per annum, the Egyptian pound being worth 6d. more than the pound sterling.

Private practice is not allowed.

It is to be distinctly understood that the appointment gives no claim to pension or indemnity.

The Government reserves to itself the right to dismiss the Assistant for misconduct or incapacity.

In the Government Schools, as in all State Administrations in Egypt, Sunday is a working day. The Schools are closed on Fridays.

Leave will be granted on the same terms as to other Government Officials. The possibility of taking leave, and the period of the year at which it is granted, depend upon the exigencies of the service.

Pay commences from date of arrival in Cairo. On taking up his duties in Cairo, the Assistant will receive one month's pay in lieu of passage money.

All applicants should attach a certificate from a legally qualified Medical man, stating that, in his opinion, the candidate would pass a first-class life for insurance purposes.

All applicants should state—

Their training and qualifications in Analytical Chemistry, Their age,

What foreign languages they know, and

If they can be in Cairo by October 1st.

The latest Mail by which applications may be posted will leave London on FRIDAY, AUGUST 31st. Applications to be addressed THE DIRECTOR, Government School of Medicine, Cairo, Egypt.

THE CHEMICAL NEWS.

VOL. XCIV., No. 2437.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

YORK, 1906.

INAUGURAL ADDRESS OF THE PRESIDENT,
Prof. E. RAY LANKESTER, M.A., LL.D., D.Sc., F.R.S.,
F.L.S., Director of the Natural History Departments
of the British Museum.

(Continued from p. 56).

Physiology of Plants and Animals.—Since I have only time to pick the most important advances in each subject for brief mention, I must signalise in regard to the physiology of plants the better understanding of the function of leaf-green or chlorophyll due to Pringsheim, and to the Russian Timiriaseff, the new facts as to the activity of stomata in transpiration discovered by Horace Brown, and the fixation of free nitrogen by living organisms in the soil, and by organisms (*Bacillus radicola*) parasitic in the rootlets of leguminous plants, which thus benefit by a supply of nitrogenous compounds which they can assimilate.

Great progress in the knowledge of the chemistry of the living cells or protoplasm of both plants and animals has been made by the discovery of the fact that ferments or enzymes are not only secreted externally by cells, but exist active and preformed *inside* cells. Büchner's final conquest of the secret of the yeast-cell by heroic mechanical methods—the actual grinding to powder of these already very minute bodies—first established this, and now successive discoveries of intracellular ferments have led to the conclusion that it is probable that the cell respire by means of a respiratory "oxydase," builds up new compounds and destroys existing ones, contracts and accomplishes its own internal life by ferments. Life thus (from the chemical point of view) becomes a chain of ferment actions. Another most significant advance in animal physiology has been the sequel (as it were) of Bernard's discovery of the formation of glycogen in the liver, a substance not to be excreted, but to be taken up by the blood and lymph, and in many ways more important than the more obvious formation of bile which is thrown out of the gland into the alimentary canal. It has been discovered that many glands, such as the kidney and pancreas and the ductless glands, the suprarenals, thyroid, and others, secrete indispensable products into the blood and lymph. Hence, myxœdema, exophthalmic goitre, Addison's disease, and other disorders have been traced to a deficiency or excess of internal secretions from glands formerly regarded as interesting but unimportant vestigial structures. From these glands have in consequence been extracted remarkable substances on which their peculiar activity depends. From the suprarenals a substance has been extracted which causes activity of all those structures which the sympathetic nerve system can excite to action; the thyroid yields a substance which influences the growth of the skin, hair, bones, &c.; the pituitary gland, an extract which is a specific urinary stimulant. Quite lately the mammalian ovary has been shown by Starling to yield a secretion which influences the state of nutrition of the uterus and mammæ. Had I time, I might say a great deal more on topics such as these—topics of almost infinite importance; but the fact is that the mere enumeration of the most important lines of progress in any one science would occupy us for hours.

Nerve-physiology has made immensely important advances. There is now good evidence that all excitation of

one group of nerve-centres is accompanied by the *concurrent inhibition* of a whole series of groups of other centres, whose activity might interfere with that of the group excited to action. In a simple reflex flexure of the knee the motor-neurones to the flexor muscles are excited, but concurrently the motor-neurones to the extensor muscles are thrown into a state of inhibition, and so equally with all the varied excitations of the nervous system controlling the movements and activities of the entire body.

The discovery of the continuity of the protoplasm through the walls of the vegetable cell by means of connecting canals and threads is one of the most startling facts discovered in connection with plant-structure, since it was held twenty years ago that a fundamental distinction between animal and vegetable structure consisted in the boxing-up or encasement of each vegetable cell-unit in a case of cellulose, whereas animal cells were not so imprisoned, but freely communicated with one another. It perhaps is on this account the less surprising that lately something like sense-organs have been discovered on the roots, stems, and leaves of plants, which, like the otocysts of some animals, appear to be really "statocytes," and to exert a varying pressure according to the relations of these parts of the plant to gravity. There is apparently something resembling a perception of the incidence of gravity in plants which reacts on irritable tissues, and is the explanation of the phenomena of geotropism. These results have grown out of the observations of Charles Darwin, followed by those of F. Darwin, Haberlandt, and Nemec.

A few words must be said here as to the progress of our knowledge of cell-substance, and what used to be called the protoplasm question. We do not now regard protoplasm as a chemical expression, but, in accordance with von Mohl's original use of the word, as a structure which holds in its meshes many and very varied chemical bodies of great complexity. Within these twenty-five years the "centrosome" of the cell-protoplasm has been discovered, and a great deal has been learnt as to the structure of the nucleus and its remarkable stain-taking bands, the chromosomes. We now know that these bands are of definite fixed number, varying in different species of plants and animals, and that they are halved in number in the reproductive elements—the spermatozoid and the ovum—so that on union of these two to form the fertilised ovum (the parent cell of all the tissues), the proper specific number is attained. It has been pretty clearly made out by cutting up large living cells—unicellular animals—that the body of the cell alone, without the nucleus, can do very little but move and maintain for a time its chemical status. But it is the nucleus which directs and determines all definite growth, movement, secretion, and reproduction. The simple protoplasm, deprived of its nucleus, cannot form a new nucleus—in fact, can do very little but exhibit irritability. I am inclined to agree with those who hold that there is not sufficient evidence that any organism exists at the present time which has not both protoplasm and nucleus—in fact, that the simplest form of life at present existing is a highly complicated structure—a nucleated cell. That does not imply that simpler forms of living matter have not preceded those which we know. We must assume that something more simple and homogeneous than the cell, with its differentiated cell-body or protoplasm, and its cell kernel or nucleus, has at one time existed. But the various supposed instances of the survival to the present day of such simple living things—described by Haeckel and others—have one by one yielded to improved methods of microscopic examination, and proved to be differentiated into nuclear and extra-nuclear substance.

The question of "spontaneous generation" cannot be said to have been seriously revived within these twenty-five years. Our greater knowledge of minute forms of life, and the conditions under which they can survive, as well as our improved microscopes and methods of experiment and observation, have made an end of the arguments and instances of supposed abiogenesis. The accounts which

have been published of "radiobes," minute bodies arising in fluids of organic origin when radium salts have been allowed to mix in minute quantities with such fluids, are wanting in precision and detail, but the microscopic particles which appear in the circumstances described seem to be of a nature identical with the minute bodies well known to microscopists, and recognised as crystals modified by a colloid medium. They have been described by Rainey, Harting, and Ord, on different occasions, many years ago. They are not devoid of interest, but cannot be considered as having any new bearing on the origin of living matter.

Psychology.—I have given a special heading to this subject because its emergence as a definite line of experimental research seems to me one of the most important features in the progress of science in the past quarter of a century. Thirty-five years ago we were all delighted by Fechner's psycho-physical law, and at Leipzig I, with others of my day, studied it experimentally in the physiological laboratory of that great teacher, Carl Ludwig. The physiological methods of measurement (which are the physical ones) have been more and more widely, and with guiding intelligence and ingenuity, applied since those days to the study of the activities of the complex organs of the nervous system which are concerned with "mind" or psychic phenomena. Whilst some enthusiasts have been eagerly collecting ghost stories and records of human illusion and fancy, the serious experimental investigation of the human mind, and its forerunner the animal mind, has been quietly but steadily proceeding in truly scientific channels. The science is still in an early phase—that of the collection of accurate observations and measurements—awaiting the development of great guiding hypotheses and theories. But much has been done, and it is a matter of gratification to Oxford men that through the liberality of the distinguished electrician, Mr. Henry Wilde, F.R.S., a lectureship of Experimental Psychology has been founded in the University of Oxford, where the older studies of Mental and Moral Philosophy, Logic, and Metaphysics have so strong a hold, and have so well prepared the ground for the new experimental development. The German investigators, W. Wundt, G. E. Müller, C. Stumpf, Ebbinghaus, and Munsterberg, have been prominent in introducing laboratory methods, and have determined such matters as the elementary laws of association and memory, and the perceptions of musical tones and their relations. The work of Goldschneider on "the muscular sense," of von Frey on the cutaneous sensations, are further examples of what is being done.

The difficult and extremely important line of investigation, first scientifically treated by Braid under the name "Hypnotism," has been greatly developed by the French school, especially by Charcot. The experimental investigation of "suggestion," and the pathology of dual consciousness and such exceptional conditions of the mind, has been greatly advanced by French observers.

The older work of Ferrier and Hitzig on the functions of the parts of the brain has been carried further by Goldz and Munk in Germany, and by Schäfer, Horsley, and Sherington in England.

The most important general advance seems to be the realisation that the mind of the human adult is a social product; that it can only be understood in relation with the special environment in which it develops, and with which it is in perpetual interaction. Professor Baldwin, of Princeton, has done important work on this subject. Closely allied is the study of what is called "the psychology of groups," the laws of mental action of the individual as modified by his membership of some form of society. French authors have done valuable work here.

These two developments of psychology are destined to provide the indispensable psychological basis for Social Science, and for the anthropological investigation of mental phenomena.

Hereafter, the well-ascertained laws of experimental psychology will undoubtedly furnish the necessary scientific

basis of the art of education, and psychology will hold the same relation to that art as physiology does to the art of medicine and hygiene.

There can be little doubt, moreover, of the valuable interaction of the study of physical psychology and the theories of the origin of structural character by natural selection. The relation of the human mind to the mind of animals, and the gradual development of both, is a subject full of rich stores of new material, yielding conclusions of the highest importance, which has not yet been satisfactorily approached.

I am glad to be able to give wider publicity here to some conclusions which I communicated to the Jubilee volume of the Société de Biologie of Paris in 1899. I there discussed the significance of the great increase in the size of the cerebral hemispheres in recent, as compared with Eocene Mammals, and in Man as compared with Apes, and came to the conclusion that "the power of building up appropriate cerebral mechanism in response to individual experience," or what may be called "educability," is the quality which characterises the larger cerebrum, and is that which has led to its selection, survival, and further increase in volume. The bearing of this conception upon questions of fundamental importance in what has been called genetic psychology is sketched as follows:—

"The character which we describe as 'educability' can be transmitted; it is a congenital character. But the results of education can not be transmitted. In each generation they have to be acquired afresh. With increased 'educability' they are more readily acquired, and a larger variety of them. On the other hand, the nerve mechanisms of instinct are transmitted, and owe their inferiority as compared with the results of education to the very fact that they are not acquired by the individual in relation to his particular needs, but have arisen by selection of congenital variation in a long series of preceding generations."

"To a large extent the two series of brain-mechanisms, the 'instinctive' and the 'individually acquired,' are in opposition to one another. Congenital brain-mechanisms may prevent the education of the brain and the development of new mechanisms specially fitted to the special conditions of life. To the educable animal the less there is of specialised mechanism transmitted by heredity, the better. The loss of instinct is what permits and necessitates the education of the receptive brain."

"We are thus led to the view that it is hardly possible for a theory to be further from the truth than that expressed by George H. Lewes and adopted by George Romanes, namely, that instincts are due to 'lapsed' intelligence. The fact is that there is no community between the mechanisms of instinct and the mechanisms of intelligence, and that the latter are later in the history of the development of the brain than the former, and can only develop in proportion as the former become feeble and defective." (From the Jubilee volume of the Soc. de Biol. of Paris, 1899; reprinted in *Nature*, 1900, vol. lxi, pp. 624, 625).

Darwinism.—Under the title "Darwinism" it is convenient to designate the various work of biologists tending to establish, develop, or modify Mr. Darwin's great theory of the origin of species. In looking back over twenty-five years it seems to me that we must say that the conclusions of Darwin as to the origin of species by the survival of selected races in the struggle for existence are more firmly established than ever. And this because there have been many attempts to gravely tamper with essential parts of the fabric as he left it, and even to substitute conceptions for those which he endeavoured to establish, at variance with his conclusions. These attempts must, I think, be considered as having failed. A great deal of valuable work has been done in consequence; for honest criticism, based on observation and experiment, leads to further investigation, and is the legitimate and natural mode of increase of scientific knowledge. Amongst the attempts to seriously modify Darwin's doctrine may be cited that to

assign a great and leading importance to Lamarck's theory as to the transmission by inheritance of newly "acquired" characters, due chiefly to American palæontologists and to the venerated defender of such views, who has now closed his long life of great work, Mr. Herbert Spencer; that to attribute leading importance to the action of physiological congruity and incongruity in selective breeding, which was put forward by another able writer and naturalist who has now passed from among us, Dr. George Romanes; further, the views of de Vries as to discontinuity in the origin of new species, supported by the valuable work of Mr. Bateson on discontinuous variation; and, lastly, the attempt to assign a great and general importance to the facts ascertained many years ago by the Abbé Mendel as to the cross-breeding of varieties and the frequent production (in regard to certain characters in certain cases) of pure strains rather than of breeds combining the characters of both parents. On the other hand, we have the splendid series of observations and writings of August Weismann, who has, in the opinion of the majority of those who study this subject, rendered the Lamarckian theory of the origin and transmission of new characters altogether untenable, and has, besides, furnished a most instructive, if not finally conclusive, theory or mechanical scheme of the phenomena of Heredity in his book "The Germ-plasm." Professor Karl Pearson and the late Professor Weldon—the latter so early in life and so recently lost to us—have, with the finest courage and enthusiasm in the face of an enormous and difficult task, determined to bring the facts of variation and heredity into the solid form of statistical statement, and have organised, and largely advanced in, this branch of investigation which they have termed "Biometrics." Many naturalists throughout the world have made it the main object of their collecting and breeding of insects, birds, and plants, to test Darwin's generalisations, and to expand the work of Wallace in the same direction. A delightful fact in this survey is that we find Mr. Alfred Russel Wallace (who fifty years ago conceived the same theory as that more fully stated by Darwin) actively working and publishing some of the most convincing and valuable works on Darwinism. He is still alive, and not merely well, but pursuing his work with vigour and ability. It was chiefly through his researches on insects in South America and the Malay Islands that Mr. Wallace was led to the Darwinian theory, and there is no doubt that the study of insects, especially of butterflies, is still one of the most prolific fields in which new facts can be gathered in support of Darwin and new views on the subject tested. Prominent amongst naturalists in this line of research has been, and is, Edward Poulton of Oxford, who has handed on to the study of entomology throughout the world the impetus of the Darwinian theory. I must here also name a writer who, though unknown in our laboratories and museums, seems to me to have rendered very valuable service in later years to the testing of Darwin's doctrines and to the bringing of a great class of organic phenomena within the cognisance of those naturalists who are especially occupied with the problems of Variation and Heredity. I mean Dr. Archdall Reid, who has with keen logic made use of the immense accumulation of material which is in the hands of medical men, and has pointed out the urgent importance of increased use by Darwinian investigators of the facts as to the variation and heredity of that unique animal, man, unique in his abundance, his reproductive activity, and his power of assisting his investigator by his own record. There are more observations about the variation and heredity of man and the conditions attendant upon individual instances than with regard to any other animal. Medical men need only to grasp clearly the questions at present under discussion in order to be able to furnish with ease data absolutely invaluable in quantity and quality. Dr. Archdall Reid has in two original books full of insight and new suggestions, the "Present Evolution of Man" and "Principles of Heredity," shown a new path for investigators to follow.

The attempt to resuscitate Lamarck's views on the in-

heritance of acquired* characters has been met not only by the demand for the production of experimental proof that such inheritance takes place, which has never been produced, but on Weismann's part by a demonstration that the reproductive cells of organisms are developed and set aside from the rest of the tissues at so early a period that it is extremely improbable that changes brought about in those other tissues by unaccustomed incident forces can be communicated to the germ-cells so as to make their appearance in the offspring by heredity. Apart from this, I have drawn attention to the fact that Lamarck's first and second laws (as he terms them) of heredity are contradictory the one of the other, and therefore may be dismissed. In 1891 I wrote:—

"Normal conditions of environment have for many thousands of generations moulded the individuals of a given species of organism, and determined as each individual developed and grew "responsive" quantities in its parts (characters); yet, as Lamarck tells us, and as we know, there is in every individual born a potentiality which has not been extinguished. Change the normal conditions of the species in the case of a young individual taken to-day from the site where for thousands of generations its ancestors have responded in a perfectly defined way to the normal and defined conditions of environment; reduce the daily or the seasonal amount of solar radiation to which the individual is exposed; or remove the aqueous vapour from the atmosphere; or alter the chemical composition of the pabulum accessible; or force the individual to previously unaccustomed muscular effort or to new pressures and strains; and (as Lamarck bids us observe), in spite of all the long-continued response to the earlier normal specific conditions, the innate congenital potentiality shows itself. The individual under the new quantities of envionring agencies shows *new* responsive quantities in those parts of its structure concerned, new or *acquired* characters.

"So far, so good. What Lamarck next asks us to accept, as his 'second law,' seems not only to lack the support of experimental proof, but to be inconsistent with what has just preceded it. The new character which is *ex hypothesi*, as was the old character (length, breadth, weight of a part) which it has replaced—a response to environment, a particular moulding or manipulation by incident forces of the potential congenital quality of the race—is, according to Lamarck, all of a sudden raised to extraordinary powers. The new or freshly acquired character is declared by Lamarck and his adherents to be capable of transmission by generation; that is to say, it alters the potential character of the species. It is no longer a merely responsive or reactive character, determined quantitatively by quantitative conditions of the environment, but becomes fixed and incorporated in the potential of the race, so as to persist when other quantitative external conditions are substituted for those which originally determined it. In opposition to Lamarck, one must urge, in the first place, that this thing has never been shown experimentally to occur; and in the second place, that there is no ground for holding its occurrence to be probable, but, on the contrary, strong reason for holding it to be improbable. Since the old character (length, breadth, weight) had not become fixed and congenital after many thousands of successive generations of individuals had developed it in response to environment, but gave place to a new character when new conditions operated on an individual (Lamarck's first law), why should we suppose that the new character is likely to become fixed after a much shorter time of responsive existence, or to escape the operation of the first law? Clearly there is no reason (so far as Lamarck's statement goes) for any such supposition, and the two so-called laws of Lamarck are at variance with one another."

In its most condensed form my argument has been stated thus by Professor Poulton:—Lamarck's "first law assumes that a past history of indefinite duration is powerless to

* I use the term "acquired" without prejudice in the sense given to that word by Lamarck himself.

reate a bias by which the present can be controlled ; while the second assumes that the brief history of the present can readily raise a bias to control the future" (*Nature*, 1894, vol. li., p. 127).

An important light is thrown on some facts which seem at first sight to favour the Lamarckian hypothesis by the consideration that, though an "acquired" character is not transmitted to offspring as the consequence of the action of external agencies determining the "acquirement," yet the tendency to react exhibited by the parent is transmitted, and if the tendency is exceptionally great a false suggestion of a Lamarckian inheritance can readily result. This inheritance of "variation in tendencies to react" has a wide application, and has led me to coin the word "educability" as mentioned in the section of this address on Psychology.

The principle of physiological selection advocated by Dr. Romanes does not seem to have caused much discussion, and has been unduly neglected by subsequent writers. It was ingenious, and was based on some interesting observations, but has failed to gain support.

The observations of de Vries—showing that in cultivated varieties of plants a new form will sometimes assert itself suddenly, and attain a certain period of dominance, though not having been gradually brought into existence by a slow process of selection—have been considered by him, and by a good many other naturalists, as indicating the way in which new species arise in *Nature*. The suggestion is a valuable one if not very novel, but a great deal of observation will have to be made before it can be admitted as really having a wide bearing upon the origin of species. The same is true of those interesting observations which were first made by Mendel, and have been resuscitated and extended with great labour and ingenuity by recent workers, especially in this country by Bateson and his pupils. If it should prove to be true that varieties when crossed do not, in the course of eventual inter-breeding, produce intermediate forms as hybrids, but that characters are either dominant or recessive, and that breeds result having pure unmixed characters—we should, in proportion as the Mendelian law is shown to apply to all tissues and organs and to a majority of organisms, have before us a very important and determining principle in all that relates to heredity and variation. It remains, however, to be shown how far the Mendelian phenomenon is general. And it is, of course, admitted on all sides that, even were the Mendelian phenomenon general and raised to the rank of a law of heredity, it would not be subversive of Mr. Darwin's generalisations, but probably tend to the more ready application of them to the explanation of many difficult cases of the structure and distribution of organisms.

Two general principles which Mr. Darwin fully recognised appear to me to deserve more consideration and more general application to the history of species than he had time to give to them, or than his followers have accorded to them. The first is the great principle of "correlation of variation," from which it follows that, whilst natural selection may be favouring some small and obscure change in an unseen group of cells—such as digestive, pigmentary or nervous cells, and that change a change of selective value—there may be, indeed often is, as we know, a correlated or accompanying change in a physiologically related part of far greater magnitude and prominence to the eye of the human onlooker. This accompanying or correlated character has no selective value, is not an adaptation—is, in fact, a necessary but useless by-product. A list of a few cases of this kind was given by Darwin, but it is most desirable that more should be established. For they enable us to understand how it is that specific characters, those seen and noted on the surface by systematists, are not in most cases adaptations of selective value. They also open a wide vista of incipient and useless developments which may suddenly, in their turn, be seized upon by ever watchful natural selection and raised to a high pitch of growth and function.

The second, somewhat but by no means altogether neglected, principle is that a good deal of the important variation in both plants and animals is not the variation of a minute part or confined to one organ, but has really an inner physiological basis, and may be a variation of a whole organic system or of a whole tissue expressing itself at several points and in several shapes. In fact, we should perhaps more generally conceive of variation as not so much the accomplishment and presentation of one little mark or difference in weight, length, or colour, as the expression of a tendency to vary in a given tissue or organ in a particular way. Thus we are prepared for the rapid extension and dominance of the variation if once it is favoured by selective breeding. It seems to me that such cases as the complete disappearance of scales from the integument of some osseous fishes, or the possible retention of three or four scales out of some hundreds present in nearly allied forms, favour this mode of conceiving of variation. So also does the marked tendency to produce membranous expansions of the integument in the bats, not only between the digits and from the axilla, but from the ears and different regions of the face. Of course, the alternative hairy or smooth condition of the integuments both in plants and animals is a familiar instance in which a tendency extending over a large area is recognised as that which constitutes the variation. In smooth or hairy varieties we do not postulate an individual development of hairs subjected one by one to selection and survival or repression.

Disease.—The study of the physiology of unhealthy, injured, or diseased organisms is called pathology. It necessarily has an immense area of observation, and is of transcending interest to mankind who do not accept their diseases unresistingly and die as animals do, so purifying their race, but incessantly combat and fight disease, producing new and terrible forms of it, by their wilful interference with the earlier rule of *Nature*.

Our knowledge of disease has been enormously advanced in the last quarter of a century, and in an important degree our power of arresting it, by two great lines of study going on side by side, and originated, not by medical men nor physiologists in the narrow technical sense, but by naturalists, a botanist, and a zoologist. Ferdinand Cohn, Professor of Botany in Breslau, by his own researches and by personal training in his laboratory, gave to Robert Koch the start on his distinguished career as a bacteriologist. It is to Metschnikoff the zoologist and embryologist that we owe the doctrine of phagocytosis and the consequent theory of immunity now so widely accepted.

We must not forget that in this same period much of the immortal work of Pasteur on hydrophobia, of Behring and Roux on diphtheria, and of Ehrlich and many others to whom the eternal gratitude of mankind is due, has been going on. It is only some fifteen years since Calmette showed that if cobra poison were introduced into the blood of a horse in less quantity than would cause death, the horse would tolerate with little disturbance after ten days a full dose, and then day after day an increasing dose, until the horse without any inconvenience received an injection of cobra poison large enough to kill thirty horses of its size. Some of the horse's blood being now withdrawn was found to contain a very active antidote to cobra poison—what is called an antitoxin. The procedure and preparation of the antitoxin is practically the same as that previously adopted by Behring in the preparation of the antitoxin of diphtheria poison. Animals treated with injections of these antitoxins are immune to the poison itself when subsequently injected with it, or if already suffering from the poison (as, for instance, by snake-bite), are readily shown by experiment to be rapidly cured by the injection of the appropriate antitoxin. This is, as all will admit, an intensely interesting bit of biology. The explanation of the formation of the antitoxin in the blood and its mode of antagonising the poison is not easy. It seems that the antitoxin is undoubtedly formed from the corresponding toxin or poison, and that the antagonism can be best understood as a chemical reaction by which the

complex molecule of the poison is upset, or effectively modified.

The remarkable development of Metschnikoff's doctrine of phagocytosis during the past quarter of a century is certainly one of the characteristic features of the activity of biological science in that period. At first ridiculed as "Metschnikoffism," it has now won the support of its former adversaries.

For a long time the ideal of hygienists has been to preserve man from all contact with the germs of infection, to destroy them, and destroy the animals conveying them, such as rats, mosquitoes, and other flies. But it has now been borne in upon us that, useful as such attempts are, and great as is the improvement in human conditions which can thus be effected, yet we cannot hope for any really complete or satisfactory realisation of the ideal of escape from contact with infective germs. The task is beyond human powers. The conviction has now been arrived at that, whilst we must take every precaution to diminish infection, yet our ultimate safety must come from within—namely, from the activity, the trained, stimulated, and carefully guarded activity of these wonderful colourless amœba-like corpuscles whose use was so long unrecognised, but has now been made clear by the patiently continued experiments and arguments of Metschnikoff, who has named them "phagocytes." The doctrine of the activity and immense importance of these corpuscles of the living body which form part of the all-pervading connective tissues and float also in the blood, is in its nature and inception opposed to what are called the "humoral" and "vitalistic" theories of resistance to infection. Of this kind were the beliefs that the *liquids* of the living body have an inherent and somewhat vague power of resisting infective germs, and even that the mere living quality of the tissues was in some unknown way antagonistic to foreign intrusive disease-germs.

The first eighteen years of Metschnikoff's career, after his under-graduate course, were devoted to zoological and embryological investigations. He discovered many important facts, such as the alternation of generations in the parasitic worm of the frog's lung—*Ascaris nigrovenosa*—and the history of the growth from the egg of sponges and medusæ. In these latter researches he came into contact with the wonderfully active cells, or living corpuscles, which in many low forms of life can be seen by transparency in the living animal. He saw that these corpuscles (as was indeed already known) resemble the well-known amœba, and can take into their soft substance (protoplasm) at all parts of their surface any minute particles and digest them, thus destroying them. In a transparent water-flea Metschnikoff saw these amœba-like, colourless, floating blood-corpuscles swallowing and digesting the spores of a parasitic fungus which had attacked the water-fleas, and was causing their death. He came to the conclusion that this is the chief, if not the whole, value of these corpuscles in higher as well as lower animals, in all of which they are very abundant. It was known that when a wound bringing in foreign matter is inflicted on a vertebrate animal the blood-vessels become gorged in the neighbourhood and the colourless corpuscles escape through the walls of the vessels in crowds. Their business in so doing, Metschnikoff showed, is to eat up the foreign matter, and also to eat up and remove the dead, wounded tissue. He therefore called these white or colourless corpuscles "phagocytes," the eater-cells, and in his beautiful book on Inflammation, published twenty years ago, proved the extreme importance of their activity. At the same time he had shown that they eat up intrusive bacteria and other germs; and his work for the last twenty years has mainly consisted in demonstrating that they are the chief, and probably the only, agents at work in either ridding the human body of an attack of disease-causing germs or in warding off even the commencement of an attack, so that the man or animal in which they are fully efficient is "immune"—that is to say, cannot be effectively attacked by disease-germs.

Disease-germs, bacteria, or protozoa produce poisons

which sometimes are too much for the phagocytes, poisoning them and so getting the upper hand. But, as Metschnikoff showed, the training of the phagocytes by weak doses of the poison of the disease-germ, or by weakened cultures of the disease-germ itself, brings about a power of resistance in the phagocytes to the germ's poison, and thus makes them capable of attacking the germs and keeping them at bay. Hence the value of inoculations.

The discussion and experiments arising from Metschnikoff's demonstrations have led to the discovery of the production by the phagocytes of certain exudations from their substance which have a most important effect in weakening the resistance of the intrusive bacteria and rendering them easy prey for the phagocyte. These are called "sensitisers," and have been largely studied. They may be introduced artificially into the blood and tissues so as to facilitate the work of the phagocytes, and no doubt it is a valuable remedial measure to make use of such sensitisers as a treatment. Dr. Wright considers that such sensitisers are formed in the blood and tissues independently of the phagocytes, and has called them "opsonins," under which name he has made most valuable application of the method of injecting them into the body so as to facilitate the work of the phagocytes in devouring the hostile bacteria of various diseases. Each kind of disease-producing microbe has its own sensitiser or opsonin; hence there has been much careful research and experiment required in order to bring the discovery to practical use. Metschnikoff himself holds and quotes experiments to show that the "opsonins" are actually produced by the phagocytes themselves. That this should be so is in accordance with some striking zoological facts, as I pointed out nearly twenty years ago. For the lowest multicellular animals provided with a digestive sac or gut, such as the polyps, have that sac lined by digestive cells which have the same amœboid character as "phagocytes," and actually digest to a large extent by swallowing or taking into their individual protoplasm raw particles of food. Such particles are enclosed in a temporary cavity, or vacuole, into which the cell-protoplasm secretes digestive ferment and other chemical agents. Now there is no doubt that such digestive vacuoles may burst and so pour out into the polyp's stomach a digestive juice which will act on food particles outside the substance of the cells, and thus by the substitution of this process of outpouring of the secretion for that of ingestion of food particles into the cells we get the usual form of digestion by juices secreted into a digestive cavity. Now this being certainly the case in regard to the history of the original phagocytes lining the polyp's gut, it does not seem at all unlikely, but on the contrary in a higher degree probable, that the phagocytes of the blood and tissues should behave in the same way, and pour out sensitisers and opsonins to paralyse and prepare their bacterial food. And the experiments of Metschnikoff's pupils and followers show that this is undoubtedly the case. Whether there is any great variety of, and difference between, "sensitisers" and "opsonins" is a matter which is still the subject of active experiment. Metschnikoff's conclusion, as recently stated in regard to the whole progress of this subject, is that the phagocytes in our bodies should be stimulated in their activity in order successfully to fight the germs of infection. Alcohol, opium, and even quinine, hinder the phagocytic action; they should therefore be entirely eschewed or used only with great caution where their other and valuable properties are urgently needed. It appears that the injection of blood-serum into the tissues of animals causes an increase in the number and activity of the phagocytes, and thus an increase in their resistance towards pathogenic germs. Thus Durham (who was a pioneer in his observations on the curious phenomena of the "agglutination" of blood corpuscles in relation to disease) was led to suggest the injection of sera during surgical operations, and experiments recently quoted by Metschnikoff seem to show that the suggestion was well founded. Both German and French surgeons have employed the method with successful results, and the demon-

stration that an immense number of microbes are thus taken up and destroyed by the multiplication (due to their regular increase by cell division) of the phagocytes of the injected patient. After years of opposition bravely met in the pure scientific spirit of renewed experiment and demonstration, Metschnikoff is at last able to say that the foundation stone of the hygiene of the tissues—the thesis that our phagocytes are our arms of defence against infective germs—has been generally accepted.

Another feature of the progress of our knowledge of disease—as a scientific problem—is the recent recognition that minute animal parasites of that low degree of unicellular structure to which the name "Protozoa" is given, are the causes of serious and ravaging diseases, and that the minute alga-like plants, the bacteria, are not alone in possession of this field of activity. It was Laveran—a French medical man—who, just about twenty-five years ago, discovered the minute animal organism in the red blood-corpuscles, which is the cause of malaria. Year by year ever since our knowledge of this terrible little parasite has increased. We now know many similar to, but not identical with it, living in the blood of birds, reptiles, and frogs.

It is the great merit of Major Ross, formerly of the Indian Army Medical Staff, to have discovered, by most patient and persevering experiment, that the malaria parasite passes a part of its life in the spot-winged gnat or mosquito (*Anopheles*), not, as he had first supposed, in the common gnat or mosquito (*Culex*), and that if we can get rid of spot-winged mosquitoes or avoid their attentions, or even only prevent them from sucking the blood of malarial patients, we can lessen, or even abolish, malaria.

This great discovery was followed by another as to the production of the deadly "Nagana" horse and cattle disease in South Africa by a screw-like, minute animal parasite, the *Trypanosoma Drucei*. The Tsetse fly, which was already known in some way to produce this disease, was found by Colonel David Bruce to do so by conveying by its bite the *Trypanosoma* from wild big game animals, to the domesticated horses and cattle of the colonists. The discovery of the parasite and its relation to the fly and the disease was as beautiful a piece of scientific investigation as biologists have ever seen. A curious and very important fact was discovered by Bruce—namely, that the native big game (zebras, antelopes, and probably buffaloes), are *tolerant* of the parasite. The *Trypanosoma* grows and multiplies in their blood, but does not kill them or even injure them. It is only the unaccustomed introduced animals from Europe which are poisoned by the chemical excreta of the *Trypanosomes* and die in consequence. Hence the wild creatures—brought into a condition of tolerance by natural selection and the dying out of those susceptible to the poison—form a sort of "reservoir" of deadly *Trypanosomes* for the Tsetse flies to carry into the blood of new-comers. The same phenomenon of "reservoir-hosts" (as I have elsewhere called them) has since been observed in the case of malaria; the children of the native blacks in Africa and in other malarious regions are *tolerant* of the malarial parasite, as many as 80 per cent of children under ten being found to be infected, and yet not suffering from the poison. This is not the same thing as the immunity which consists in *repulsion* or *destruction* of the parasite.

The *Trypanosomes* have acquired a terrible notoriety within the last four years, since another species, also carried by a Tsetse fly of another species, has been discovered by Castellani in cases of sleeping sickness in Uganda, and demonstrated by Colonel Bruce to be the cause of that awful disease. Over 200,000 natives of Uganda have died from it within the last five years. It is incurable, and, sad to relate, not only a certain number of European employes have succumbed to it in tropical Africa, but a brave young officer of the Army Medical Corps, Lieutenant Tulloch, has died from the disease acquired by him in the course of investigation of this disease and its possible cure, which he was carrying out, in association with other

men of science, on the Victoria Nyanza Lake in Central Africa. Lieutenant Tulloch was sent out to this investigation by the Royal Society of London, and I will venture to ask you to join that body in sympathy for his friends, and admiration for him and the other courageous men who risk their lives in the endeavour to arrest disease.

Trypanosomes are now being recognised in the most diverse regions of the world as the cause of disease—new horse diseases in South America, in North Africa, in the Philippines and East India are all traced to peculiar species of *Trypanosome*. Other allied forms are responsible for Delhi-sore, and certain peculiar Indian fevers of man. A peculiar and ultra-minute parasite of the blood cells causes Texas fever, and various African fevers deadly to cattle. In all these cases, as also in that of plague, the knowledge of the carrier of the disease, often a mite or acarid—in that of plague the flea of the rat—is extremely important, as well as the knowledge of reservoir-hosts when such exist.

The zoologist thus comes into closer touch than ever with the profession of medicine, and the time has arrived when the professional students of disease fully admit that they must bring to their great and hopeful task of abolishing the diseases of man the fullest aid from every branch of biological science. I need not say how great is the contentment of those who have long worked at apparently useless branches of science, in the belief that all knowledge is good, to find that the science they have cultivated has become suddenly and urgently of the highest practical value.

I have not time to do more than mention here the effort that is being made by combined international research and co-operation to push further in our knowledge of phthisis and of cancer, with a view to their destruction. It is only since our last meeting at York that the parasite of Phthisis or Tubercle has been made known; we may hope that it will not be long before we have similar knowledge as to Cancer. Only eighteen months have elapsed since Fritz Schaudinn discovered the long-sought parasitic germ of Syphilis, the *Spirocheta pallida*. As I write these words the sad news of Schaudinn's death at the age of thirty-five comes to me from his family at Hamburg—an irreparable loss.

Let me finally state, in relation to this study of disease, what is the simple fact—namely, that if the people of Britain wish to make an end of infective and other diseases they must take every possible means to discover capable investigators, and employ them for this purpose. To do this far more money is required than is at present spent in that direction. It is necessary, if we are to do our utmost, to spend a thousand pounds of public money on this task where we now spend one pound. It would be reasonable and wise to expend ten million pounds a year of our revenues on the investigation and attempt to destroy disease. Actually, what is so spent is a mere nothing, a few thousands a year. Meanwhile our people are dying by thousands of preventable disease.

To be continued.)

Non-existence of Phosphorus Trisulphide.—R. Boulouch.—Several chemists refuse to regard phosphorus trisulphide, P_2S_3 , as a definite compound, chiefly because its distillation gives products of different composition. Further, its mixed constitution appears to result from the fact that its fusion, which takes place a little below 200° , ought not to be total till over 300° . The author makes a series of investigations on the nature of this substance, and finds definitely that there do not exist any definite phosphorus sulphides having formulæ between P_4S_3 and P_3S_5 , and, consequently, there can be no phosphorus trisulphide. He also states that P_3S_5 is not necessarily a definite compound.—*Comptes Rendus*, cxliii., No. I.

ADDRESS TO THE CHEMICAL SECTION
OF THE
BRITISH ASSOCIATION.
YORK, 1906.

By Prof. WYNDHAM DUNSTAN, M.A., LL.D., F.R.S., F.C.S.,
President of the Section.

SOME IMPERIAL ASPECTS OF APPLIED CHEMISTRY.

THE President of the Chemical Section of the British Association must always have a large choice of subjects for his Address. He may attempt to review the chemical progress of the year, or to give an account of researches in that division of the science in which he is most interested. He may deal with the ever-recurring problems of education; or, again, he may draw attention to the importance of our science in one or other of its many relations to National and Imperial affairs. I have decided to adopt the last course, and to invite your attention at York, where several tropical products furnish the basis of important industries, to the intimate connection of our science with the problems that await solution in connection with the utilisation of the raw materials and economic products of our Colonies, and especially those of our tropical Possessions. There is a pressing need that the Imperial Government should recognise much more fully than it has hitherto done, and at least as fully as foreign Governments are already doing, the claims of scientific investigation to be regarded as the pioneer instrument of this work, and as the essential first step in the material and commercial development of our Possessions.

Although my remarks will be chiefly directed to the importance of chemistry in this connection, my plea will be more general. It is that the scientific method of experimental research should be systematically applied in each division of the sciences concerned. In the case of raw materials, however, whether vegetable or mineral, their commercial value must depend chiefly, if not entirely, upon their composition, and sooner or later the method of chemistry must therefore be applied.

In determining the value of the mineral resources of a country other specialists are also concerned, and the assistance of the geologist, the mineralogist, and eventually of the metallurgist may be required. Similarly with vegetable and agricultural products the services of the economic botanist and the entomologist will be needed. It will therefore be necessary for me in dealing with the subject as a whole to touch upon several aspects in which other sciences are concerned, and with which the science of chemistry must co-operate in attaining a practical end—namely, the material development of the countries concerned. I need make no apology for many allusions to scientific agriculture, for this subject is this year attached to this Section, and indeed the science of chemistry is of fundamental importance to agricultural practice both at home and in the tropics.

In the first place I must ask you to allow me to say a few words as to the very wide interests that are involved in the proper solution of the problem of colonial development.

It is all-important that the wage-earning community of this country should have an adequate supply of tea, coffee, cocoa, rice, tobacco, and other commodities, and that our manufacturers should be able to count upon a regular supply of cotton, jute, rubber, and other raw materials as far as possible under their own control. All these products are derived almost exclusively from the tropics, and experience shows that it is a great disadvantage to the manufacturer not to be able to exercise control in the direction of securing the regular production of these materials, and especially not to be able to avoid the great and sudden fluctuations in their price, which are often the result of financial speculation on the part of a foreign capitalist who has secured the control of the output of a foreign country.

The almost entire dependence of the great textile indus-

tries of Lancashire upon the cotton crop of the Southern States of America has placed this industry at the mercy of American speculators, whose tactics may lead, as in 1903, to such a rise in the price of the raw material as to render it imperative for the manufacturer to close his mills, and by throwing large numbers out of employment to bring poverty and misery to many thousands of people.

The great principle which must now necessarily guide our system of administration and expenditure in our tropical Colonies and Protectorates has as its purpose the utilisation of natural resources and the creation and development of native industries with the aid of European supervision and advice. Adequate supplies of produce, natural and agricultural, will thus be ensured to British manufacturers and consumers from territories within the administration of the British Crown. This principle of employing our "undeveloped estates" for the advantage of our manufacturers and consumers, and at the same time for the benefit of the natives who inhabit these countries, was put into action by Mr. Chamberlain during his long tenure of office as Secretary of State for the Colonies, and this recognition of a vitally important principle must always be associated with his name.

Excepting India and the self-governing Colonies, the Crown Colonies and Protectorates, for which alone the Imperial Government is directly responsible, include an area of about two and a-half million square miles and a population of about forty millions. The value of these possessions to us at the present time may be judged from the value of their import and export trade with the United Kingdom. The value of the exports of these countries in 1904 was estimated at about four and a-half million pounds sterling, and the imports from the United Kingdom at about twelve and a-half million pounds sterling. In gauging the importance to this country of the development of these Possessions, the export trade of which is only in its infancy, it should be remembered that the profits arising from the export as well as from the import trade are chiefly domiciled in this country, since practically the whole of this trade is in the hands of British merchants, and the entire profits, including those of shipping, &c., are therefore subject to our national system of taxation, and represent a very substantial annual contribution to the British Exchequer.

It is therefore only reasonable that a certain sum should be expended from British funds to aid the applications of science to the commercial development of these Possessions. Such an expenditure in the light of the facts to which I have drawn attention may be regarded as an investment with the certainty of a profitable return.

I have thought it necessary to give this brief account of the position of our still undeveloped Crown Colonies and Protectorates and the national importance to us of their systematic development before proceeding to the principal subject of this Address, which is to emphasize the aid which science in several of its branches can render to this work of development, and especially the science of chemistry, the capacities of which in this connection have so far not been sufficiently recognised.

The importance of utilising our own tropical Possessions as sources of the raw material required by the manufacturer is now generally recognised, and very considerable progress has been made in recent years. The tea produced in India and Ceylon has largely superseded the China tea formerly used in this country. Similarly, coffee is extensively grown in India, in the West Indies, and in several of our African Possessions. The jute cultivation in India has been very successful, and the demand for this fibre is so great that the question of its cultivation in our West African Colonies is now under consideration. Indiarubber, hitherto chiefly obtained from South America, is of increasing importance as a commercial article, and the South American tree has been introduced with success in Ceylon, the Straits Settlements, and the Federated Malay States, which are rapidly becoming important rubber-producing countries, whose produce is competing success-

fully with that of South America. The cultivation of cotton, hitherto principally carried on in the United States, is being vigorously proceeded with in India, the West Indies, and in West Africa, as well as in Egypt and the Sudan, and we may look forward in the future to these countries supplying the British manufacturer with a large proportion, if not the whole, of the cotton he requires.

There are, however, vast resources, both mineral and vegetable, in our Colonies and Protectorates which are awaiting development for an exact knowledge of their composition and properties, which can only be ascertained by scientific means and chiefly through chemical investigation, whilst the British manufacturer is in need of increased and better supplies of the raw materials on which his industrial activity depends. This demand for increased supplies now affects nearly every industry in this country. Rubber and fibres are well-known examples; oils and fats for the manufacture of soap and perfumes; and tanning materials, as well as numerous minerals, are other instances in which our manufacturers are at present anxious to discover new sources of supply. These sources can only be discovered and their value ascertained by properly directed scientific investigations.

We have heard much recently respecting the assistance which science can bring to the maintenance and development of the industrial efficiency of this country, and the Imperial Government is being urged to give its help especially by providing increased facilities for the education of scientific men, competent to aid the manufacturers of this country in improving their methods and processes. In this work the science of chemistry is one of the most important. There is scarcely an industry to which it is not able to render immense service. Within recent years this fact has slowly gained recognition, and the principle of State assistance to industry is virtually admitted, both in respect of education and of research. The most recent examples of a recognition of the principle are the grants made from the National Treasury to the new Technological College at South Kensington and to the National Physical Laboratory.

Not less important than the service which science can render to existing industries and their extension is that which it can contribute to the Imperial problem of ascertaining and rendering available for the manufacturer the vast undeveloped resources of our own Possessions. Our own experience and the example of other countries have shown that such work cannot be systematically carried on by private enterprise. Upon its successful accomplishment depends, not only the unrestricted supply of the necessary raw materials for which the manufacturer looks in increasing quantity, but also the prosperity of the country which produces these materials. This success can only be brought about by a combined effort on the part of the manufacturer and of the Government. The manufacturer can provide information as to the materials he needs. The preliminary work of discovering suitable material by scientific means, as several foreign Governments have already recognised, must be endowed, directed, and carried on with Imperial funds. It cannot be expected that private enterprise will take steps to explore the resources of little-known countries on the chance of a particular material being discovered, nor can the work, as a rule, be successfully done by this means. Experience shows that the most effective manner of promoting the commercial development of a new country is for the Government to carry out systematically with its own officers the preliminary work of exploration and examination of the natural resources, with the aid of such technical advice as may be necessary from manufacturers and users, and then, having established the fact that particular products of value can be found or cultivated in a given country, to leave commercial enterprise to do the rest. By action on these lines immense progress is being made in French, German, and Dutch Possessions, whilst the United States Government has taken similar action with the Philippines. In our own case, where this work exists it is in most cases in a more or less

embryonic condition, and lacks the organisation which is necessary for success.

In many of our Crown Colonies and Protectorates there already exist, or are in the process of organisation, agricultural and other scientific departments, many of which include officers who are engaged in the work of exploring and developing the vegetable resources of these countries especially by experimental planting. Chemists are attached to some, but not to all of these departments. In the West Indies the valuable work accomplished by Professor Harrison, Mr. Francis Watts, Professor Albuquerque, Professor Carmody, and Mr. Cousins is well known, and illustrates the great services which the science of chemistry may render, not only to tropical agriculture, but to every branch of economic development. It is clearly desirable that at least one scientific department should be attached to the Government of each of the principal Crown Colonies and Protectorates. As a rule, it is convenient that this should be an agricultural department with the services of a scientific chemist at its disposal. In a tropical climate, and with limited appliances at his command, it must be admitted that a chemist is severely handicapped, and, as a rule, he cannot be expected at first to be able to do much beyond the comparatively simple and preliminary work, chiefly analytical, which, however, in a little known country is of the greatest importance to an agricultural department. In addition, he would have to deal with the composition of natural products of all kinds, both vegetable and mineral, as well as with the improvement of native industries. If the chemist is able to refer complicated or special investigations to a central department at home, and is provided with assistance in the routine work, he would be in a position to undertake the scientific investigation of a selection from the numerous problems with which a chemist will be confronted.

A chemist working in the spirit of an investigator will be able to render special services to the cause of tropical agriculture, and it is therefore of importance that in future the men appointed to these posts should be chosen as far as possible on account of the promise they have shown as investigators. The determination of the constituents of little known indigenous plants as the first step towards ascertaining their economic value is another department of work which cannot be carried out without a chemist, and the same applies to the examination of poisonous plants, and also of minerals, in addition to the determination of the composition of foods and feeding stuffs.

Tropical agriculture is a subject which is now of the first importance, especially in those countries in which our policy is to depend on a native population for the actual cultivation of the soil. We have two functions to perform in our position as supervisors; the one is to ascertain the nature and capabilities of the soil by actual experiment, for which well-organised experimental stations are a necessary part of every agricultural department; the other duty is to convey to the natives, chiefly by means of demonstration, the results of this experimental work, so that they may be persuaded to make it a part of their agricultural practice.

Work on these lines is being done under Government auspices in the French and German Colonies, and I may allude to the French successes in Algeria, in Senegal, and in the Sudan, and to the advances made by Germany in East Africa. These achievements are mainly due to a policy of continuous scientific work on agricultural lines. We shall have the privilege of hearing from Dr. Greshoff, the eminent director of the Colonial Museum at Haarlem, an account of the chemical investigations which are being carried out in connection with Java and the Dutch East Indies.

In many of our own Colonies and Protectorates active agricultural departments, equipped with the means of experimental working, are only now in process of organisation. One of the most recently organised of these is that of the Transvaal, which, at Lord Milner's initiation, has been completely equipped on the lines of that model for all

such effort, the agricultural department of the United States. This department has as its chief chemist Mr. Herbert Inglis, of the Yorkshire College, now the University of Leeds.

If we are to compete successfully with foreign countries it is necessary that the position of science in relation to tropical agriculture should be definitely recognised. The days when a botanical garden served the purpose of an entire scientific establishment in a Colony have passed away, and we now require, in order that a proper return should be obtained, and the natives assisted in their agricultural practice, a scientific department with a proper complement of specially trained officers, including a consulting chemist, other specialists being added to the staff as the requirements arise. These officers should be remunerated on a scale likely to attract some of the best educated men from this country, which is at present far from being the case.

It would be out of place to discuss here the detailed organisations of these scientific departments. I merely desire to urge the necessity of their functions being extended, and to their receiving adequate financial support.

It is important that the scientific work which is being accomplished by these various departments should be brought to a focus, and that the results obtained in one Colony should be available for the information of the departments in other Colonies. The work of all such establishments requires to be unified by co-operation with a Central Department which can extend the investigations conducted in the Colonies, carry out investigations and inquiries which cannot be undertaken on the spot, maintain the necessary touch with the manufacturers, and co-ordinate the work undertaken and the results obtained in each of the separate Colonial establishments and systematically collate it, so that each may be aware of the results that are being obtained in other countries. In our African Possessions at present the same investigations and inquiries have to be conducted independently, and often without the knowledge that the problem in question has been already solved.

Another increasingly urgent duty of the Central Department is to inform the Colonial establishments of the results of the work which is being conducted in foreign countries, and of the progress which is being made in the utilisation of raw materials all over the world, and to bring to their notice the constantly changing requirements of the manufacturers and users of raw materials.

So far as botany is concerned, this co-ordination has been to a large extent effected through the agency of the Royal Gardens, Kew, which is in touch, through the Colonial Office, with all the botanical gardens in the Crown Colonies and Protectorates. In chemistry, as well as in certain other subjects, these duties have been performed in recent years by the Scientific and Technical Department of the Imperial Institute, which is now working in co-operation, not only with the Governments of the Crown Colonies and Protectorates, but also with those of several of the self-governing Colonies, and also with the Scientific Departments, which have been brought into existence in India, where at last the importance of scientific agriculture is receiving due recognition from the Government.

So little has hitherto been done in this direction that the number of problems requiring attention is exceedingly large; and even with a specially trained staff of workers and extensive laboratories, such as now exist at the Imperial Institute, it becomes necessary to select as the principal subjects for investigation those which are regarded by the Governments of the countries concerned as of the most practical importance and in which the British manufacturer is at the moment most concerned. There must therefore remain a large number of materials of unknown composition, and of problems of purely scientific interest which offer an attractive field for the chemical investigator. Already steps have been taken to provide for the investigation of these subjects by scientific men who

are willing to undertake them in communication with the Institute. For example, Mr. A. G. Perkin, F.R.S., has been furnished with material which has led to the identification and determination of the constitution of the colouring matters of a number of plants which are employed as dyes in India and the Colonies. Professor A. H. Church, F.R.S., has determined the composition of many new or little known food grains. Dr. Crossley, Mr. Le Sueur, and Dr. Lewkowitsch have examined the constituents of a large number of fats and oils furnished by seeds of Indian and African origin. Dr. W. J. Russell, F.R.S., has been furnished with selected materials for examination in connection with his interesting investigations of those substances which affect the photographic plate in the dark, whilst the Hon. R. J. Strutt, F.R.S., has investigated the radio-activity of a number of new or little known minerals containing rare earths. Last year over five hundred different materials and problems were submitted from the Colonies and India for investigation to the Scientific Department of the Imperial Institute, and each year there must remain an increasing number of interesting subjects which cannot be included in the Department's annual programme of work. Many of these would furnish excellent subjects for chemical research by advanced students in connection with the universities and technical colleges throughout the country. It is nearly always possible to arrange to furnish the necessary material for any competent worker to deal with. Next year a list of such subjects awaiting investigation will be available at the Imperial Institute for those in search of subjects for chemical research.

Whilst the investigation of some of these subjects may at once produce results of scientific value, many of them present difficulties in their investigation which are far more serious than those which attend the usual synthetical work in organic chemistry. I do not know of any more profitable experience for the advanced student who is already familiar with the principles of organic chemistry and of laboratory practice than the separation in the pure state of the chemical constituents of a plant and the determination of their chemical constitution. In inorganic chemistry the examination of a new mineral furnishes similar experience.

In carrying out research of the kind I am advocating, the chemical investigator will have the additional advantage of knowing that the scientific results he obtains will contribute to the knowledge of the resources of the British Empire, and possibly be the means of laying the foundations of new industries.

I need hardly remind chemists that some of the most important discoveries in our science, and many of those which have had the most profound influence on the development of chemical theory, have arisen from the examination of the constituents of raw materials. The discovery of morphia in opium led to the recognition of the new class of alkaloids; the discovery of amygdalin in the bitter almond of the new group of glucosides; the investigation by Liebig and Wöhler of the chemical properties and composition of the essential oil of the bitter almond was largely instrumental in laying the foundations of modern organic chemistry; whilst it was during the examination of the constituents of bran that Fownes was led to the discovery of furfural and the subsequent recognition of a new type of organic compound. In more recent times, the examination of the constituents of oil of turpentine and various essential oils yielded by different plants has been the means of elucidating the chemical theory of the great group of terpenes, and latterly Harries' investigation of caoutchouc has led to the discovery of the ozonides, which seem likely to be of much importance as a new means of determining the constitution of certain classes of organic compounds. Lastly, I may remind you that the discovery of helium might have been long delayed had not Professor Miers drawn Sir William Ramsay's attention to the so-called nitrogen furnished by the mineral cleveite.

(To be continued).

NOTES OF A COURSE OF LECTURES ON THE
OLD AND NEW CHEMISTRY.†II. EXTRACTS FROM DIFFERENT AUTHORS RELATING TO
THE NEW CHEMISTRY.

By Prof. Sir JAMES DEWAR, F.R.S., &c.

(Concluded from p. 58).

Later Phases of Chemical Progress.—Dewar.

1. FARADAY'S Law of Electro-chemical Decomposition; Mechanical Equivalent of Heat (Joule, Mayer); Carnot's Theory of the Motive Power of Heat; Conservation of Energy (Joule, Mayer, and Helmholtz); Absolute Thermometric Scale and Measurement of Electro-Motive Forces (Kelvin); Thermal Effects of Fluids in Motion (Joule and Kelvin).

2. Avogadro distinction of Atoms and Molecules; Radical Theory; Organic Substitution; Organo-Metallic Bodies; Idea of Structure; Classification; Vegetable and Animal Chemistry; Analogy between Inorganic and Organic Chemistry (Work of Wöhler, Liebig, Dumas, Laurent, Gerhardt).

3. Addition of Twenty-five new Elements; New Atomic Weights; Atomicity of the Elements; Tetra Atomicity of Carbon Basis of Organic Chemistry; Periodic Law of the Distribution of Atomic Weights (Newlands, Mendeleeff); Prediction and Discovery of Missing Elements (Mendeleeff); Correction of Atomic Weights; Extension of the Law to the Physical Properties of the Elements and Compounds.

4. Dissociation and the Law of Chemical Equilibrium; Density of Vapours and High Temperatures (Deville); Application of Thermo-dynamical Laws to Chemical Interaction; Measurement of the Energy of Reactions; Thermal Chemistry; Temperature of Flame; Pressure of Gaseous Reactions; Study of Explosives; Phase Rule (Gibbs); Mass in Relation to Chemical Action.

5. Spectrum Analysis (Bunsen and Kirchhoff); Discovery of New Elements; Solar and Stellar Chemistry; Spectra of the Elements; Tables of Wave Lengths (Angstrom and Thalen); Ultra Violet and Infra Red Spectra; Universal Distribution of the Earth Elements; Spectroscopic and Chemical Analysis of Meteorites; The Laws of Series in Line and Band Spectra; Photographic and Phosphorescent Actions.

6. Liquid and Gaseous Diffusion; Occlusion and the Nature of Crystalloids and Colloids (Graham); Solid Solution; Eutectic Mixtures; Constitution of Alloys; Continuity of the Gaseous and Liquid States of Matter (Andrews); Generalised Equation of the Gaseous Laws (Van der Waals).

7. Theory of Solution; Osmotic Pressure; Electrolytic Dissociation; Electric Conductivity; Ionic Hypothesis; Atomic Electricity; Solution Molecular Weights; Number of Molecules entering into a Reaction; Velocity of Chemical Change (Work of Raoult, Arrhenius, Van't Hoff, Oswald).

8. Development of Organic Synthesis; Benzene Ring (Kekulé); Position Theory; Coal Tar Colours; Artificial Formation of Sugars; Pyridine Ring; Alkaloids like Conia and Nicotin; Colouring Matters like Alizarin and Indigo; Albumen Derivatives like the Polypeptides.

9. Fermentation (Pasteur); Bacteria, Enzymes, Toxins, and Antitoxins; Zymase; Dextra and Lævo Rotation in Organic Bodies; The Asymmetric Carbon Atom; Stereo-Chemistry.

10. Liquid Air and the Command of Low Temperatures; Solid Hydrogen; Nadir of steady Temperature of -258° C.; Charcoal at Low Temperatures as Agent of Research; Properties of Matter near the Zero of Absolute Temperature; Hydrogen not a Metal; Electric Furnace; Metallic Carbides and Hydrides; Synthesis of Hydrocarbons; Industrial Production of Cyanamide and Nitric Acid; Industrial Electrolysis of Fuse Salts; Metals as Fuel; Artificial Minerals.

* Delivered at the Royal Institution, May 26th, 1906.

11. Fourth state of Matter (Crookes); Electric Discharge in High Vacua; Röntgen Radiation; Radio-Activity of Uranium (Becquerel); Isolation of Polonium and Radium (Professor and Madame Curie); Heat Evolution of Radium; Rate of Energy Emission in Radio-Active Bodies a Constant; Luminosity of Radium; Emanations of Radium; Electrical, Photographic, and Fluorescent Effects; Atomic Disintegration; Seven Transformation Products of Radium; Helium Constituent of Decomposition Products of the Radium Atom; Thorium and Actinium Emanations; Emanation in Active Gases.

12. Electrons; Corpuscles; Structure of the Atom; Electrical Basis of Matter.

The Future of Chemistry.

"The most important uses of natural objects are not those which offer themselves to us most obviously. The chief use of the moon for man's immediate purposes remained unknown to him for five thousand years from his creation. And, since it cannot but be that innumerable and most important uses remain to be discovered among the materials and objects already known to us, as well as among those which the progress of science must hereafter disclose, we may hence conceive a well-grounded expectation, not only of constant increase in the physical resources of mankind, and the consequent improvement of their condition, but of continual accessions to our power of penetrating into the arcana of nature, and becoming acquainted with her highest laws." (Herschel).

CORRESPONDENCE.

ON THE

CONDENSATION PRODUCTS OF α -NAPHTHOL
AND BENZOPHENONE CHLORIDE.*To the Editor of the Chemical News.*

SIR,—The products obtained by the condensation of benzophenone chloride with α -naphthol, mentioned by A. G. Shrimpton, B.Sc., in the CHEMICAL NEWS of July 13th (vol. xciv., p. 13), were described in a paper entitled "Condensation of Benzophenone Chloride with α - and β -Naphthols" in the *Trans. Chem. Soc.*, 1906, lxxxix., 771).—I am, &c.,

G. W. CLOUGH.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 1, July 2, 1906.

Action of Sulphuretted Hydrogen on certain Metallic and Metalloidal Oxides. Application to Volcanic Phenomena and Thermal Waters.—Armand Gautier.—The author investigates the action of sulphuretted hydrogen in presence of Fe_2O_3 , Al_2O_3 , H_2O , CO , CO_2 , SiO_2 , &c., at the high temperatures of the interior of the earth.

Certain Synthetic Reactions of Pinacolone.—Louis Henry.—Hitherto pinacolone has never been investigated in its capacity as a ketone, $(\text{H}_3\text{C})_2\text{C}=\text{CO}-\text{CH}_3$, and in synthetic reactions. It lends itself to the latter in a remarkable manner. The author investigates its action on magnesium methyl bromide and cyanhydric acid, and all his experiments confirm the ketone nature of pinacolone. It is remarkable both from its origin and its properties.

Phosphorus Chloronitride.—MM. Besson and Rosset.—Phosphorus chloronitride can be prepared by the action of heat on $\text{PCl}_5 \cdot 8\text{NH}_3$, but only in very small quantities. Water reacts upon it, and the action is the best and most rapid in sealed tubes at $150-200^\circ$:— $(\text{PCl}_2\text{N})_3 + 12\text{H}_2\text{O} = 6\text{HCl} + 3\text{PO}_4\text{H}_3 + 3\text{NH}_3$. Oxygen has no action upon it, but during the formation of ozone the nitrogen products react slightly upon it, forming a brownish yellow solid, the composition of which has not yet been determined. Nitrogen peroxide has the following reaction: $2(\text{PCl}_2\text{N})_3 + 4\text{NO}_2 = 2\text{N}_2\text{O} + \text{NOCl} + \text{P}_2\text{O}_5 + 3\text{Cl} + \text{N}$.

Isomorphism of Mercuric Iodide with Zinc and Cadmium Iodides.—A. Duboin.—Mercuric iodide will crystallise in all proportions with the iodides of zinc and cadmium; this fact constituting an interesting new case of isomorphism.

Crystallography of Iron.—F. Osmond and G. Cartaud.—The authors continue their investigations on the subject of the crystallography of iron, and now investigate manganese steel after tempering it in water.

Determination of the Transformation-points of certain Steels by the Method of Electric Resistance.—P. Fournel.—The method of electric resistance allows of the determination of the critical points of the five specimens of steel examined, containing varying proportions of carbon, silicon, and manganese.

Solubility of Carbon in Calcium Carbide.—H. Morel Kahn.—The author heats in an electric furnace a mixture of lime and sugar-charcoal. The carbide obtained is crystalline and is attacked by water. If the residue is washed with pure hydrochloric, nitric, and hydrofluoric acid, and then well with water, graphite remains, which contains a variable but very small quantity of carbon silicide as an impurity.

Action of Urethane and Urea on Ethyl Glyoxylate. New Synthesis of Allantoin.—L. J. Simon and G. Chavanne.—When ethyl glyoxylate acts upon urethane, it gives diurethane-glyoxylic ether, $\text{CO}_2\text{C}_2\text{H}_5-\text{NH}-\text{CH}=\text{CO}_2\text{C}_2\text{H}_5$. When the same substance is condensed with urea, the product obtained, when analysed, consists of a hitherto unknown ethyl allantolate, $\text{NH}_2-\text{CO}-\text{NH}-\text{CH}=\text{CO}_2\text{C}_2\text{H}_5$.

Formation of Indazylic Derivatives of *o*-Hydrazobenzoic Acid.—P. Carré.

Ethyl Dioximidosuccinate.—A. Wahl.—The author makes a series of experiments on the constitution of ethyl dioximidosuccinate.

A Method of Reaction of certain Anhydrides of Acids. New Series of Acids having a Pyranic Radicle.—R. Fosse.—The anhydrides of certain acids produce with the hydroxyl derivatives of dinaphthopyrane and of xanthane a curious result, which the author proceeds to investigate.

New Method of Estimating the Casein in Cheese.—A. Trillat and M. Sauton.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are names of the Officers and Committee of Section B (Chemistry) at the York Meeting of the British Association:—

President—Prof. Wyndham R. Dunstan, M.A., LL.D., F.R.S.

Vice-Presidents—G. T. Beilby, F.R.S.; Hofrat Dr. H. Caro; Prof. A. Haller; A. Vernon Harcourt, F.R.S.; Prof. Dr. A. Liebermann; Com.-Rat Dr. von Martius; Prof. P. van Romburgh; Sir William H. Perkin, F.R.S.; Prof. A. Smithells, F.R.S.; Prof. W. A. Tilden, F.R.S.

Secretaries—Prof. W. J. Pope, F.R.S. (Recorder); Dr. E. F. Armstrong; Prof. A. W. Crossley, D.Sc., Ph.D.; S. H. Davies.

Committee—Prof. H. E. Armstrong, F.R.S.; Dr. Barger; W. Barlow; Dr. P. P. Bedson; Prof. E. Divers, F.R.S.; Prof. H. B. Dixon, F.R.S.; Prof. J. J. Dobbie, F.R.S.; T. Fairley; Prof. A. G. Green; Dr. Greshoff; A. D. Hall, M.A.; Prof. G. G. Henderson, D.Sc.; Dr. T. A. Henry; Francis Jones; Dr. A. Lapworth; Dr. Bevan Lean; S. Leetham; Dr. Le Sueur; D. A. Louis; Dr. T. M. Lowry; Dr. H. Marshall, F.R.S.; Prof. H. A. Miers, F.R.S.; Dr. D. H. Nagel; Prof. M. A. Parker; Prof. A. G. Perkin, F.R.S.; Prof. W. H. Perkin, F.R.S.; H. Ramage, M.A.; Sir W. Ramsay, F.R.S.; Rev. A. W. Richards; H. Richardson, M.A.; J. Smyth, M.A.; J. Spiller; Prof. J. J. Sudborough; Dr. J. F. Thorpe; G. Ward.

The Papers brought before the Section were as follows:—

Presidential Address.

S. Leetham and W. Cramp—The Electrical Discharge in Air and its Applications.

Prof. van Romburgh—The 1:3:5-Hexatrien.

Dr. T. M. Lowry—Report on Dynamic Isomerism.

Prof. A. W. Crossley—Report on Hydro-aromatic Substances.

G. Barger and F. H. Carr—Note on Ergot Alkaloids.

A. Vernon Harcourt—Effect upon the Concentration of a Solution of the presence of an Excess of Undissolved Salt.

G. Beilby—Crystallisation of Gold in the Solid State.

Prof. H. A. Miers and Miss F. Isaac—Temperature at which Water Freezes in Sealed Tubes.

Discussion on the Production of Prussic Acid by Plants. (Papers contributed by the President, Dr. Henry, Prof. van Romburgh, Dr. Greshoff, and others).

Dr. Greshoff—Chemical Research in the Dutch East Indies.

T. Jamieson—Utilisation of Nitrogen in Air by Plants.

A. D. Hall and C. T. Gimmingham—Action of Ammonium Salts upon Clay and kindred Substances.

Francis V. Darbishire and Dr. E. J. Russell—Oxidation in Soils and its Relation to Productiveness.

S. S. Pickles—Report on the Present Position of the Chemistry of Rubber.

Prof. Carl Herries (Kiel)—Constitution of Caoutchouc.

Prof. W. A. Tilden—Polymerisation of Isoprene.

Prof. W. A. Tilden—Constituents of *Dyera Costulata*.

H. H. Robinson—Report on the Present Position of the Chemistry of Gums.

H. H. Robinson—On a Gum (*Cochlospermum Gossypium*) which produces Acetic Acid on Exposure to Air.

R. J. Caldwell—Report on the Hydrolysis of Sugars.

W. Poppellwell Bloxam—Method of Determining Indigotin. The Factors which determine Minimal Diet Values. (Joint Discussion with Section I. Opened by Dr. F. Gowland Hopkins).

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

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DIAMONDS.

A Lecture delivered before the British Association at Kimberley.

By SIR WILLIAM CROOKES,

Hon. D.Sc. (Oxford, Dublin, and Cape of Good Hope), F.R.S.

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SESSION OF 1906-7.

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All applicants should state—

Their training and qualifications in Analytical Chemistry,

Their age,

What foreign languages they know, and

If they can be in Cairo by October 1st.

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THE CHEMICAL NEWS.

VOL. XCIV., No. 2438.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

YORK, 1906.

INAUGURAL ADDRESS OF THE PRESIDENT,
Prof. E. RAY LANKESTER, M.A., LL.D., D.Sc., F.R.S.,
F.L.S., Director of the Natural History Departments
of the British Museum.

(Concluded from p. 66).

II. *The Advancement of Science as Measured by the Support given to it by Public Funds, and the Respect accorded to Scientific Work by the British Government and the Community at large.*

WHILST I have been able, though in a very fragmentary and incomplete way, to indicate the satisfactory and, indeed, the wonderful progress of science since this Association last met in York, so far as the making of new knowledge is concerned, I am sorry to say that there is by no means a corresponding "advancement" of Science in that signification of the word which implies the increase of the influence of science in the life of the community, the increase of the support given to it, and of the desire to aid in its progress, to discover and then to encourage and reward those who are specially fitted to increase scientific knowledge, and to bring it to bear so as to promote the welfare of the community. I am speaking on a privileged occasion to a body of men who are met together for the Advancement of Science, and I claim the right to say to them without offence to the representatives of institutions which I criticise, what is in my mind.

It is, unfortunately, true that the successive political administrators of the affairs of this country, as well as the permanent officials, are altogether unaware to-day, as they were twenty-five years ago, of the vital importance of that knowledge which we call science, and of the urgent need for making use of it in a variety of public affairs. Whole departments of Government in which scientific knowledge is the one thing needful are carried on by ministers, permanent secretaries, assistant secretaries, and clerks who are wholly ignorant of science, and naturally enough dislike it since it cannot be used by them, and is in many instances the condemnation of their official employment. Such officials are, of course, not to be blamed, but rather the general indifference of the public to the unreasonable way in which its interests are neglected.

A difficult feature in treating of this subject is that when one mentions the fact that ministers of State and the officials of the public service are not acquainted with science, and do not even profess to understand its results or their importance, one's statement of this very obvious and notorious fact is apt to be regarded as a personal offence. It is difficult to see wherein the offence lies, for no one seeks to blame these officials for a condition of things which is traditional and frankly admitted.

This is really a very serious matter for the British Association for the Advancement of Science to consider and deal with. We represent a line of activity, a group of professions which are in our opinion of vital importance to the well-being of the nation. We know that those interests which we value so highly are not merely ignored and neglected, but are actually treated as of no account or as non-existent by the old-established class of politicians and administrators. It is not too much to say that there is a natural fear and dislike of scientific knowledge on the part

of a large proportion of the persons who are devoid of it, and who would cease to hold, or never have held, the positions of authority or emolument which they now occupy, were scientific knowledge of the matters with which they undertake to deal required of them. This is a thorny subject, and one in which, however much one may endeavour to speak in general terms, it is difficult to avoid causing personal annoyance. Yet it seems to me one which, believing as I do that it is of most urgent importance, it is my duty as your President to press upon the attention of the members of the British Association. Probably an inquiry into, and discussion of, the neglect of science and the questionable treatment of scientific men by the administrative departments of Government, would be more appropriate to a committee appointed by the Council of the Association for this purpose than to the Presidential Address.

At the same time, I think the present occasion is one on which attention should be drawn in general terms to the fact that science is not gaining "advancement" in public and official consideration and support. The reason is, I think, to be found in the defective education, both at school and university, of our governing class, as well as in a racial dislike among all classes to the establishment and support by public funds of posts which the average man may not expect to succeed by popular clamour or class privilege in gaining for himself—posts which must be held by men of special training and mental gifts. Whatever the reason for the neglect, the only remedy which we can possibly apply is that of improved education for the upper classes, and the continued effort to spread a knowledge of the results of science and a love for it amongst all members of the community. If members of the British Association took this matter seriously to heart they might do a great deal by insisting that their sons, and their daughters too, should have reasonable instruction in science both at school and college. They could, by their own initiative and example, do a good deal to put an end to the trifling with classical literature and the absorption in athletics which is considered by too many schoolmasters as that which the British parent desires as the education of his children.

Within the past year a letter has been published by a well-known nobleman, who is one of the Trustees of the British Museum, holding up to public condemnation the method in which the system laid down by the officials of the Treasury and sanctioned by successive Governments, as to the remuneration of scientific men, was applied in an individual case. I desire to place on record here the Earl of Crawford's letter to *The Times* of October 31, 1905, for the careful consideration of the members of the British Association and their friends. When such things are done, science cannot be said to have advanced much in public consideration or Governmental support.

To the Editor of The Times.

SIR,—The death, noted by you to-day, of my dear friend and colleague Dr. Copeland, His Majesty's Astronomer for Scotland, creates a vacancy in the scientific staff of Great Britain.

Will you permit me, Sir, to offer a word of warning to any who may be asked to succeed him?

Students or masters of astronomy are not, in the selfish sense, business men, nor are they as a general rule overburdened with this world's goods. It behoves them henceforth to take more care as to their future in case of illness or physical infirmity, and not to trust to the gratitude or generous impulse of the Treasury Department.

In old days it was the custom when a man distinguished in science was brought into a high position in the Civil Service that he was credited with a certain number of years' service ranking for pension. This practice has been done away with, and a bargain system substituted. A short while ago the growing agonies of heart disease caused Dr. Copeland to feel that he was less able to carry on the duties of his post, and he

determined to resign; but he learnt that under the scale, and in the absence of any special bargain, the pension he would receive would not suffice for the necessities of life. The only increase his friends could get from the Treasury was an offer to allow him about half-a-crown a week extra by way of a house.

Indignant and ashamed of my Government, I persuaded Dr. Copeland to withdraw his resignation and to retain the official position which he has honoured till his death.

I trust, Sir, that this memorandum of mine may cause eminent men of science who are asked to enter the service of the State when already of middle age to take heed for their future welfare.—I am, Sir, your obedient servant,

CRAWFORD.

2, Cavendish Square, October 28.

It is more agreeable to me not to dwell further on the comparative failure of science to gain increased influence and support in this country, but to mention to you some instances on the other side of the account. As long ago as 1842 the British Association took over and developed an observatory in the Deer Park at Kew, which was placed at the disposal of the Association by Her Majesty the Queen. Until 1871 the Association spent annually a large part of its income—as much in later years as £600 a year in carrying on the work of the Kew Observatory, consisting of magnetic, meteorological, and physical observations. In 1871 the Association handed over the Observatory to the Royal Society, which had received an endowment of £10,000 from Mr. Gassiot for its maintenance, and had further devoted to that purpose considerable sums from its own Donation Fund and Government grant. Further aid for it was also received from private sources. From this Observatory at last has sprung, in the beginning of the present century, the National Physical Laboratory in Bushy Park, a fine and efficient scientific institution, built and supported by grants from the State, and managed by a committee of really devoted men of science who are largely representatives of the Royal Society. In addition to the value of the site and buildings occupied by the National Physical Laboratory, the Government has contributed altogether £34,000 to the capital expenditure on new buildings, fittings, and apparatus, and has further assigned a grant of £6000 a year to the working of the laboratory. This institution all men of science are truly glad to have gained from the State, and they will remember with gratitude the statesmen—the late Marquis of Salisbury, the Right Hon. Arthur J. Balfour, Mr. Haldane, and others—as well as their own leaders—Lord Rayleigh, Sir William Huggins, and the active body of physicists in the Royal Society who have carried this enterprise to completion. The British Association has every reason to be proud of its share in early days in nursing the germ at Kew which has at length expanded into this splendid national institution.

I may mention also another institution which, during the past quarter of a century, has come into existence and received, originally through the influence of the late Lord Playfair (one of the few men of science who has ever occupied the position of a Minister of the Crown), and later by the influence of the Right Hon. Joseph Chamberlain, a subsidy of £1000 a year from the Government, and a contribution of £5000 towards its initial expenses. This is the Marine Biological Association, which has a laboratory at Plymouth, and has lately expended a special annual grant, at the spontaneous invitation of His Majesty's Treasury, in conducting an investigation of the North Sea in accordance with an international scheme devised by a central committee of scientific experts. This scheme has for its purpose the gaining such knowledge of the North Sea and its inhabitants as shall be useful in dealing practically and by legislation with the great fisheries of that area. You will, perhaps, not be surprised to hear that there are persons in high positions who, though admittedly unac-

quainted with the scientific questions at issue or the proper manner of solving them, are discontented with the action of the Government in entrusting the expenditure of public money to a body of scientific men who give their services, without reward or thanks, to carrying out the purposes of the international inquiry. Strange criticisms are offered by these malcontents in regard to the work done in the international exploration of the North Sea, and a desire is expressed to secure the money for expenditure by a less scientific agency. I do not hesitate to say here that the results obtained by the Marine Biological Association are of great value and interest, and, if properly continued and put to practical application, are likely to benefit very greatly the fishery industry; on the other hand, if the work is cut short or entrusted to incompetent hands, it will no doubt be the case that what has already been done will lose its value—that is to say, will have been wasted. There is imminent danger of this perversion of the funds assigned to this scientific investigation taking place. There is no guarantee for the continuance of any funds or offices assigned to science in one generation by the officials of the next. The Mastership of the Mint held by Isaac Newton, and finally by Thomas Graham, has been abolished, and its salary appropriated by non-scientific officials. Only a few years ago it was with great difficulty that the Government of the day was prevented from assigning the Directorship of Kew Gardens to a young man of influence devoid of all knowledge of botany!

One of the most solid tests of the esteem and value attached to scientific progress by the community is the dedication of large sums of money to scientific purposes by its wealthier members. We know that in the United States such gifts are not infrequent; they are rare in this country. It is therefore with especial pleasure that I call your attention to a great gift to science in this country made only a few years ago. Lord Iveagh has endowed the Lister Institute, for researches in connection with the prevention of disease, with no less a sum than a quarter of a million pounds sterling. This is the largest gift ever made to science in this country, and will be productive of great benefit to humanity. The Lister Institute took its origin in the surplus of a fund raised by Sir James Whitehead when Lord Mayor, some sixteen years ago, for the purpose of making a gift to the Pasteur Institute in Paris, where many English patients had been treated, without charge, after being bitten by rabid dogs. Three thousand pounds was sent to M. Pasteur, and the surplus of a few hundred pounds was made the starting-point of a fund which grew, by one generous gift and another, until the Lister Institute on the Thames Embankment at Chelsea was set up on a site presented by that good and high-minded man, the late Duke of Westminster.

Many other noble gifts to scientific research have been made in this country during the period on which we are looking back. Let us be thankful for them, and admire the wise munificence of the donors. But none the less we must refuse to rely entirely on such liberality for the development of the army of science, which has to do battle for mankind against the obvious disabilities and sufferings which afflict us and can be removed by knowledge. The organisation and finance of this army should be the care of the State.

It is a fact which many of us who have observed it regret very keenly, that there is to-day a less widespread interest than formerly in natural history and general science, outside the strictly professional arena of the school and university. The field naturalists among the squires and the country parsons seem nowadays not to be so numerous and active in their delightful pursuits as formerly, and the Mechanics' Institutes and Lecture Societies of the days of Lord Brougham have given place, to a very large extent, to musical performances, bioscopes, and other entertainments, more diverting, but not really more capable of giving pleasure than those in which science was popularised. No doubt the organisation and professional character of scientific work are to a large extent the cause of this

alling-off in its attraction for amateurs. But perhaps that decadence is also due in some measure to the increased general demand for a kind of manufactured gaiety, readily sent out in these days of easy transport from the great centres of fashionable amusement to the provinces and rural districts.

In conclusion, I would say a word in reference to the associations of our place of meeting, the birthplace of our Society. It seems to me not inappropriate that a Society for the Advancement of Science should have taken its origin under the walls of York Minster, and that the clergy of the great cathedral should have stood by its cradle. It is not true that there is an essential antagonism between the scientific spirit and what is called the religious sentiment. "Religion," said Bishop Creighton, "means the knowledge of our destiny and of the means of fulfilling it." We can say no more and no less of Science. Men of Science seek, in all reverence, to discover the Almighty, the Everlasting. They claim sympathy and friendship with those who, like themselves, have turned away from the more material struggles of human life, and have set their hearts and minds on the knowledge of the Eternal.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

YORK, 1906.

By Prof. WYNDHAM DUNSTAN, M.A., LL.D., F.R.S., F.C.S.,
President of the Section.

(Concluded from p. 69).

I HAVE thought that it would be of interest on the present occasion if some account were given in the Section of the chemistry of certain of the raw materials employed in the principal manufacturing industries of the city of York. These industries are vitally concerned with an adequate supply of certain raw products of tropical origin, especially cocoa and gums. In connection with the first of these, which has hitherto been obtained chiefly from the West Indies, a new industry of cocoa production has sprung up in West Africa, notably in the Gold Coast and in Lagos. This West African cocoa presents some peculiarities which have rendered it desirable to examine the nature of its constituents. Gums of the nature of gum arabic are at present chiefly derived from the French Colony of Senegal. It is, however, clear from the examination of gum collected in West Africa that that country, and especially Northern Nigeria, will be able in the future to contribute to the needs of the British manufacturer, in addition to the Sudan, India, and Australia, which will also be able to make important contributions. In connection with the investigation of these gums derived from new sources at the Imperial Institute, the very remarkable observation has been made that certain gums from India and the Colonies possess the property of evolving acetic acid when exposed to the air. The chemical constitution of one of these gums has been fully investigated at the Imperial Institute by Mr. H. H. Robinson, who will contribute a paper on the subject to the Section, in which he will show that the production of acetic acid is due to the elimination of an acetyl group by hydrolysis through the moisture of the air. He has also succeeded in elucidating to a large extent the chemical nature of the gum. Mr. Robinson will also make a report on the present position of the chemistry of gums, a class of substances whose constitution is exceptionally difficult to unravel. Little, if any, advance has been made in recent years on the well-known researches of O'Sullivan.

There is no more important group of questions demanding attention from the chemist at the present time than those connected with the production of indiarubber or caoutchouc. An enormous increase in the demand for indiarubber has

taken place in the last few years, and last year the production was not less than 60,000 tons. Until recently the supply of rubber came chiefly from two sources—the forests of Brazil, which contain the tree known as *Hevea brasiliensis*, furnishing the Para rubber of commerce which commands the highest price, and the forests of Africa, where climbing plants, generally of the *Landolphia* class, also furnish rubber. The increased demand for caoutchouc has led to the extensive planting of the Para rubber tree, especially in Ceylon and in the Federated Malay States. Systematic cultivation and improved methods of preparation are responsible for the fact that the product of the cultivated tree, which begins to furnish satisfactory rubber when six or seven years old, is now commanding a higher price than the product of the wild tree in Brazil. It is estimated that within the next seven years the exports of cultivated indiarubber from Ceylon and the Federated Malay States will reach between ten and fifteen million pounds annually, and that after fifteen years they may exceed the exports of the so-called wild rubber from Brazil.

The services which chemistry can render to the elucidation of the problems of rubber production and utilisation are very numerous. Methods of treatment depending on a knowledge of the other constituents of the latex have led to the production of rubber in a purer condition. Much still remains to be elucidated by chemical means as to the nature of the remarkable coagulation of the latex. As is well known, the latex is a watery fluid resembling milk in appearance which contains the rubber, or, as I think more probable, the immediate precursor of rubber, together with proteids and other minor constituents. The constituent furnishing rubber is in suspension, and rises like cream when the latex is at rest. On the addition of an acid, or sometimes of alkali, or even on mere exposure, coagulation takes place and the rubber separates as a solid, the other constituents for the most part remaining dissolved in the aqueous liquid or "serum." The first view taken of the nature of the coagulation process was that, like the coagulation of milk by acids, it is dependent upon a process of proteid coagulation, the separated proteids carrying down the rubber during precipitation.

This explanation cannot, however, be considered complete by the chemist, and there are peculiarities connected with the coagulation of the latex which are opposed to the view that it is wholly explained by the coagulation of the associated proteids. The experimental investigation of the question on the chemical side is beset with many difficulties which are increased if access cannot be had to fresh latex. A number of experiments were made at the Imperial Institute with latex forwarded from India. The difficulties contended with in preventing coagulation during transit were great, but in the case of the latex derived from certain plants these were to some extent surmounted, and the results obtained, especially with reference to the behaviour of certain solvents towards the latex, led to the conclusion that "coagulation" can take place after removal of the proteids, and that in all probability it is the result of the polymerisation of a liquid which is held in suspension in the latex and on polymerisation changes into the solid colloid which we know as caoutchouc. Weber, by experiments conducted in South America with fresh latex, arrived at a similar conclusion, which later workers have confirmed. Although the nature of the process is not yet completely elucidated, there is little room for doubt that the coagulation is due to the polymerisation of a liquid and possibly of a liquid hydrocarbon contained in the latex. For the chemist the important question remains as to the nature of this liquid from which caoutchouc is formed.

The chemical nature of caoutchouc is a subject which has attracted the attention of distinguished chemists from the middle of the eighteenth century, among them being Faraday, Liebig, and Dalton. Faraday was the first to examine the constituents of the latex of *Hevea brasiliensis*. It is only in recent years that our knowledge of the constitution of organic compounds, and especially of the terpene group, has rendered it possible to make any great advance.

It is interesting to record that Greville Williams, in 1860, made most important contributions to this subject. He identified a new hydrocarbon, isoprene, as a decomposition product of caoutchouc, and recognised its polymeric relation to caoutchouc.

The results obtained from the analytical side, and especially the formation of di-pentene and isoprene by pyrogenic decomposition of caoutchouc, had pointed to the fact that caoutchouc was essentially a terpenoid polymer of the formula $C_{10}H_{16}$. Harries finds, however, that the ozonide of caoutchouc, when distilled with steam, breaks up into lævulinic aldehyde, lævulinic acid, and hydrogen peroxide, and he concludes from this that caoutchouc is a polymer of an 1 : 5 dimethyl cyclooctadien. Whilst Harries' work has brought us much nearer the goal, and has led to the discovery of a new method of investigation through the ozonides, which is obviously of wide application, it cannot yet be said that the constitution of caoutchouc has been settled or its relation to the parent substance of the latex definitely established. It has still to be shown how a closed-chain hydrocarbon such as Harries' octadien can undergo polymerisation forming the colloid caoutchouc.

There are strong arguments for the view that the constitution of the parent substance present in the latex is nearly related to that of isoprene. This remarkable hydrocarbon of the formula C_5H_8 , first obtained by Greville Williams from the dry distillation of rubber, is an unsaturated olefinic hydrocarbon which is found among the products, resulting from heating caoutchouc. It readily polymerises, forming di-pentene. Bouchardat noticed that this hydrocarbon obtained from the pyrogenic decomposition of caoutchouc furnished a substance identical with rubber when acted on by hydrochloric acid and under other conditions. To Wallach and also to Tilden is due the further important observation that when isoprene prepared from oil of turpentine is kept for some time, it gradually passes into a substance having all the characteristic properties of caoutchouc.

I have very briefly drawn attention to the present position of our knowledge of the chemistry of caoutchouc in illustration of the interest which attaches to the examination of vegetable products, and also because of the immense importance of the problem from the practical and commercial standpoint. Chemistry in this case holds the premier position in reference to this subject, and to a large extent may be said to hold the key to the future of the rubber industry in all its phases. The discovery of better methods of coagulation, preparation, and purification will be effected through chemical investigation, as will also the determination of the manner of utilising the various other plants which furnish rubber-like latices. That the physical properties of raw rubber, on which its technical value depends, are to be correlated with the chemical composition of the material there can be no doubt. The chemical analysis of raw rubber, as at present conducted, is, however, not always to be taken by itself as a trustworthy criterion of quality, and more refined processes of analysis are now needed. Although the finest caoutchouc for technical purposes is only yielded by some half-dozen plants, under whose names these varieties of caoutchouc pass, there can scarcely be a doubt that the elastic substance in each case possesses a very similar, if not identical, chemical structure. Nearly all the latices and similar fluids furnished by plants contain more or less caoutchouc. Even opium, which is the dried juice of the capsule of the poppy, contains caoutchouc, whilst the opium yielded by certain Indian species contains a notable proportion. Chemistry must determine the means by which caoutchouc can best be separated from these relatively poor latices. In view of the increasing production of the nearly pure caoutchouc which is furnished by *Hevea brasiliensis*, *Funtumia elastica*, *Castilloa elastica*, *Ficus elastica*, and a few other plants which occur or can be cultivated in several of our tropical Possessions, the question is not a pressing one at the moment.

Moreover, it cannot be doubted that chemical science will sooner or later be able to take a definite step towards the production of rubber by artificial means.

The production of caoutchouc by chemical means has, indeed, virtually been accomplished in its formation from isoprene. The exact nature of this change has still to be determined. When this has been done it will only remain to cheapen the cost of production to make the manufacture of synthetic rubber a purely practical problem. I should be the last to discourage the great extension of rubber planting which is now taking place. It is warranted by the present demand for the material. It has also to be remembered that the actual cost of producing raw rubber, which is at present about one shilling per pound, will probably be reduced, and the market price of rubber may eventually be so considerably lowered that, as with quinine, the synthetic production could not be profitably carried on. That is a question which involves many factors at present unknown, and only time can decide. Chemists may, however, confidently predict that before the British Association again meets at York the synthetic production of rubber will be a fully accomplished fact.

As I have said, our science is concerned with nearly every problem connected with the great rubber industry, and in concluding these few remarks I may allude to the production of vulcanised rubber depending on the formation of additive compounds of the hydrocarbon with sulphur. In this connection I should mention the recent experiments of Mr. Bamber in Ceylon, which appear to show that vulcanisation may be accomplished by acting on the uncoagulated latex with chloride of sulphur. If this proves to be practicable, it may mean the transference to the tropics of the subsidiary industry of vulcanisation, which is at present carried on in Europe.

Owing to the importance and interest which attach to the chemistry of rubber, it is to form an important feature in the work of this Section at the York Meeting. Papers will be contributed by some of the best known workers in this field, by Professor Tilden, and by Professor Harries, of Kiel, who will give an account of his recent work; whilst Mr. Pickles, of the Imperial Institute, will present a report summarising the whole of our chemical knowledge of the subject.

The chemical investigation of raw materials often raises, unexpectedly, problems of great scientific interest. The examination at the Imperial Institute of the seeds of the Para rubber tree (*Hevea brasiliensis*) has shown that they contain what proves to be a valuable drying oil, and in the course of the investigation it was ascertained that there is also present in the seeds an enzyme closely allied to, if not identical with, lipase, which is capable of splitting the oil by hydrolysis into glycerin and the free fatty acid. Subsequently, during the examination of other oil seeds similar enzymes have been detected, and it would appear probable that most oil seeds may prove to contain an enzyme capable of decomposing the fatty constituent.

Another subject of great chemical interest and botanical importance which has come into prominence in connection with the Indian and Colonial work of the Imperial Institute is to be included in a joint discussion which has been arranged with the Section of Botany. I refer to the production of prussic acid by plants, which, as I have elsewhere suggested, it is convenient to refer to as cyanogenesis. In this discussion we shall have the advantage of the co-operation of Professor van Romburgh and Dr. Greshoff, whose work with Dr. Treub of Java on this subject is known to chemists and botanists alike. The history of the origin of the several investigations in which Dr. Henry has been associated with me is not without interest in connection with the principal subject of this Address. During the first British expedition to the Sudan against the Mahdi a number of transport animals were poisoned through eating a small vetch which springs up in the Nile Valley during the fall of the river. The plant (*Lotus arabicus*) is well known to the Arabs, by whom it is cut when fully grown, and used as fodder for animals.

The results of the investigation of this matter which were communicated to the Royal Society proved that the young plant generated prussic acid when crushed with water. It was found to contain a new glucoside lotusin, together with an enzyme capable of decomposing it into prussic acid, dextrose, and a yellow colouring matter, lotoflavin.

The glucoside is of special chemical interest, as being the only one known which contains the cyanogen group attached in the molecule to the sugar residue. Further investigation has shown that other fodder plants which are occasionally poisonous owe this character to the existence of other cyanogenetic glucosides. In a series of papers communicated to the Royal Society, Dr. Henry and I have described the properties and constitution of dhurrin from *Sorghum vulgare*, and of phaseolunatin, which we have shown to be responsible for the production of prussic acid by *Phaseolus lunatus* (Lima beans), *Manihot utilisima* (cassava or tapioca), and by linseed (the flax plant). Phaseolunatin is remarkable in furnishing acetone as one of its products of hydrolysis. The investigation, besides fulfilling the primary purpose for which it was carried out, has raised a host of problems;—as to the constitution of glucosides, the nature of the enzymes which accompany them in the plants, and also in relation to the fundamental question of plant metabolism.

Another subject of Imperial as well as National importance is to be the subject of a joint discussion with the Section of Physiology. I refer to the problem of diet. As chemists we are interested in this subject chiefly from the point of view of the composition of foods, and of the molecular structure which is associated with dietetic value. The first attempt to deal with the matter from the scientific side was made by a great chemist, Liebig. We are now in a position to investigate the problem more minutely, and the work of American physiologists has already led to important results. We have still to learn how materials such as rice and potatoes, which are nearly free from proteids, continue nevertheless to serve as the main diet of large numbers of people. It would seem that the best plan of operations will be for physiologists to settle by the accurate methods now available the precise value of typical foodstuffs, and for the chemist to deal with these in relation to their composition, and finally with reference to the constitution of their constituents. The time has come when an advance must be made from the chemical side in the analytical methods employed for gauging the value of food materials.

I feel that I have said much, but that I have left still more unsaid on many topics. I must leave almost untouched the entire subject of mineral chemistry, which is not only important in connection with the determination of the resources of India and the Colonies, but is also a subject somewhat neglected on its chemical side, which has been recently brought into prominence through the discovery of radio-activity.

The new radio-active mineral thorinite, from Ceylon, of which Mr. Blake and I have given an account to the Royal Society, brings me at once to a subject which raises the most fundamental of chemical questions, the nature of the elements and of the atom. The recent discussions of this subject have become so purely speculative that, whilst chemistry is bound to follow the lead of physics in this matter, chemists are inclined to consider that more well-ascertained facts are needed for any further discussion to be profitable from the chemical side.

In this address I have ventured to urge the fuller recognition by Government of the scientific method as a powerful instrument in promoting the commercial development of the Colonies, and I have drawn attention to the important part the science of chemistry can play in the Imperial work of developing the resources of our Possessions.

No apology is needed in this place for directing attention to a subject which involves a most important practical application of our science, since one of the principal functions

of the British Association is to bring science into close touch with the problems of our national life, and to interest the general public in the application of science to their solution.

I have, however, also shown that many problems of the highest scientific interest arise in connection with the investigation of these economic problems.

The meeting of the British Association coincides this year with the celebration of the Jubilee of the Coal-Tar Colour Industry, and we welcome among us a number of distinguished foreign chemists who have come to join in honouring the great chemist Sir William Perkin, to whom the inception of this industry is due. It is fitting that, as President of the Chemical Section, I should refer to this great occasion in my Address, and express for myself, as well as for the chemists here present, the admiration we feel for Sir William Perkin's genius and for the splendid example he has set in his life-long devotion to experimental research, an example from which all of us have profited who have had the good fortune to come into relation with him.

CHEMICAL AND ELECTRICAL CHANGES INDUCED BY ULTRA-VIOLET LIGHT.*

By Sir WILLIAM RAMSAY and J. F. SPENCER, M.Sc., Ph.D.

1. LIGHT from an iron arc, falling on earth-connected plates of elements, placed at an angle of 45° , to the cap of an electroscope, discharges the electroscope. Even when an aluminium box, earthed, the top closed with a gold or silver leaf, so as to surround the plate of the electroscope completely, was interposed, discharge still occurred; but its rate was decreased when a thin aluminium leaf was substituted for the gold or silver. Discharge occurred when the electroscope was charged positively, but not negatively; the charge was approximately at 800 volts.

2. As the iron arc proved unsteady, a Cooper-Hewitt uvioi-glass mercury lamp was substituted. The illumination was insufficient to cause discharge through gold or silver leaf, but took place when the plate of the electroscope was exposed to the reflections. The rate of discharge caused by plates of thirty-three elements, metals and non-metals, were in the order of their position in the electric series, gold, iron, and manganese being notable exceptions. No discharge took place if the electroscope was negatively charged.

3. The rate of discharge was greatly increased, and the order was practically the same, when the plates formed part of the electroscope; in this case, however, it was necessary to charge the electroscope negatively, and again to 800 volts.

4. The sulphides of a number of the metals in the form of plates also caused discharge, but at a much slower rate; some iodides were also measured, and found to cause discharge. The order, however, is quite distinct from that of the elements.

5. The plates gave a more rapid discharge with a fresh surface; they "tired," however, and the rate of falling off presented some peculiarities. For dyad metals, the curve presents two obvious "breaks," and two phases of constant rate of "tiring;" for tetrad metals, four such stages were observed.

6. A unifluid cell, containing two identical plates of copper, cadmium, or gold, gives a small change of potential when one plate is illuminated by ultra-violet or sun-light, in a tube of uvioi glass, the other plate being kept in the dark. That chemical action has occurred was obvious on examining the exposed plate after insolation.

All these phenomena are brought into line on the hypothesis that elements and compounds, when illuminated by ultra-violet light, discharge corpuscles.

* Abstract of Paper read before the British Association (Section A), York Meeting, 1906.

DYNAMIC ISOMERISM.*

ATTENTION has been directed during the past two years mainly to the determination of the proportions in which isodynamic compounds are in equilibrium in solution. The method of investigation, which was briefly referred to in the last Report (Cambridge, 1904, p. 218; compare Lowry, *Proc.*, 1903, xix., 156), involves the measurement of the solubility of one of the isomerides, both before and after isomeric change has taken place. Only one of the solid isomerides can persist in stable equilibrium with the solution. This is not necessarily the form which predominates in the liquid; indeed, the modification which thus persists may vary with the solvent (Dr. Whiteley, *Trans.*, 1899, lxxv., 231) and differ in closely related compounds (compare nitro-camphor and its π -bromo-derivative). The concentration of the original compound is kept substantially constant by stirring the solution with an excess of the solid; any increase which is observed in the concentration of the saturated solution is attributed to the formation in the liquid of one or more dynamic isomerides. If the initial concentration of the saturated solution be A and the final concentration B, the ratio A/B affords a measure of the proportion of the original material present in the solution when equilibrium between the dynamic isomerides is attained.

In applying the method experimentally certain difficulties are encountered.

1. When isomeric change occurs rapidly, the products appear in the solution before the latter is saturated with the original material. In such cases it is necessary to make solubility-measurements at frequent intervals during the early stages of the experiment and to deduce the initial value by extrapolation. When, however, isomeric change proceeds slowly or only after the addition of a catalyst, the measurements can be made at leisure, and the experimental errors are very greatly reduced.

2. Whether isomeric change be rapid or slow, it is essential that the solid used in effecting saturation consist wholly of one isomeride. To ascertain if this be the case, the sample should be extracted at constant temperature with successive quantities of the solvent; if the material be pure, the different extracts should have equal concentrations. In comparing different series of observations, those which give the smallest ratio of initial to final concentration are the more likely to be correct.

3. In deducing the proportion of the original material present in the solution, it has been assumed that the solubility of this form remains constant throughout the experiment and is not affected by the products of isomeric change. This cannot, as a rule, be tested directly, since the method is of greatest value in cases in which the less stable isomerides are unknown or cannot be prepared in a pure state. Important evidence can be obtained, however, by studying the effect of adding to the solvent known quantities of a pure substance of allied structure. Experiments have been made on the influence of glucose on the solubility of galactose, by Mr. Robertson on the influence of β -methylglucoside on the solubility of the α -glucoside, on the influence of $\alpha\pi$ -dibromocamphor on the solubility of the $\alpha\pi$ -isomeride, and of bromocamphor π -sulphonamide on that of the β -sulphonamide: these have shown that in the case of sparingly soluble compounds of high melting-point the change of solubility is insignificant. In the case of soluble compounds of low melting-point the effects produced are no longer negligible, but the correction to be applied may be estimated by similar methods. In the most extreme case that has yet been examined the correction amounts to 2 per cent on the volume concentration or 4 per cent on the weight concentration.

Since the appearance of the last report four investigations dealing with the subject have been completed and described; briefly summarised, the results obtained are as follows:—

1. *Nitro-derivatives of Camphor* (Lowry and Robertson, *Trans.*, 1904, lxxxv., 1541).—The solubility of normal nitro-camphor in light petroleum increases in the course of a few hours in the ratio 0.82 : 1, indicating that when equilibrium is attained the normal and pseudo forms are present in the ratio 82 : 18 or 5 : 1 approximately. In the case of the π -bromo derivative, the pseudo-form is that which persists in contact with the solution: its solubility increases in the ratio 0.17 : 1; the isomerides are therefore present in the ratio 83 : 17, or (as in the case of nitro-camphor itself) 5 : 1 approximately.

2. *Glucose and Galactose* (Lowry, *Trans.*, 1904, lxxxv., 1551).—In methyl-alcoholic solutions one-half of the sugar is in the α -form, the other half probably consisting almost entirely of the stereoisomeric β -sugar. In presence of water the proportion of the α -sugar decreases: this might be due to a displacement of the equilibrium between the α and β sugars, but is more probably due to the formation of a largely increased proportion of a third form of the sugar, such as the aldehyde or its hydrate. The formation of some such intermediate compound in which the terminal carbon atom is no longer asymmetric appears to be essential to account for the optical inversion which accompanies the interconversion of the α and β sugars.

3. *Bromocamphor and Chlorocamphor* (Lowry, *Trans.*, 1906, lxxxix.).—Kipping has shown that these compounds, although stable in neutral solutions, undergo reversible isomeric change in presence of alkalis (*Proc.*, 1905, xxi., 125). This change is accompanied by an increase of solubility in the ratio 0.89 : 1; a similar increase is observed in the case of the β and π bromo-derivatives of these compounds. In the case of chlorocamphor and bromocamphor the proportions of the α -compounds in the solutions are probably somewhat greater than 89 per cent owing to the influence of the α' -compound in increasing the solubility of the α -compounds. The proportions are estimated at 91 per cent and 93 per cent respectively.

4. *Sulphonic Derivatives of Camphor* (Lowry and Magson, *Trans.*, 1906, lxxxix.).—Kipping has shown that the π -sulphonic salts derived from α -bromocamphor and α -chlorocamphor undergo reversible isomeric change in presence of a trace of free alkali (*Proc.*, 1905, xxi., 124). Solubility measurements indicate that similar changes take place in the case of the β -sulphonic salts, amides, and other derivatives, but the observations are complicated by the fact that the compounds of the $\alpha\beta$ -series are able to pass not only into stereoisomeric $\alpha'\beta$ compounds, but also into isomeric sulpholactones. A number of the latter have been examined and described.

The expenses incurred in connection with investigations described above were in part defrayed by a grant made to the Committee in 1904. It is proposed during the coming year to undertake a detailed examination of the optical properties of nitrocamphor and other compounds which exhibit dynamic isomerism in solution. In particular it is proposed to test Biot's hypothesis that anomalous rotatory dispersion is due to the presence in solution of two modifications of a substance—a suggestion which was made some years before the phenomena of dynamic isomerism were clearly understood.

Notice of Removal.—W. A. Foyle, of Cecil Court, Charing Cross Road, W.C., begs to inform his customers that he has removed to larger and more central premises at 135, Charing Cross Road, W.C., where all further communications should be addressed. The business will in future be carried on under the name of W. and G. Foyle (THE Booksellers).

* Report of the Committee, consisting of Professor H. E. Armstrong (Chairman), Dr. T. M. Lowry (Secretary), Professor Sydney Young, Dr. J. J. Dobbie, Dr. A. Lapworth, and Dr. M. O. Forster. (Drawn up by the Secretary). Read before the British Association (Section B), York Meeting, 1906.

SPECTRA OF THE
CATHODIC PHOSPHORESCENCE OF TERBIUM
AND DYSPROSIUM DILUTED IN LIME.*

By G. URBAIN.

By diluting various pure rare earths in lime and gradually varying the relative proportions of the components of the binary phosphorescent systems so obtained, it is found that the optimum of phosphorescence corresponds to mixtures in which the proportion of rare earth is of the order of the hundredth.

This observation determines the conditions in which it is convenient to work if we wish, in the course of the separations, to take phosphorescence spectra as a guide. In practice it is convenient to mix intimately by chemical means, from 1 to 3 m.grms. of the rare earth with about 1 grm. of pure lime.

When we examine in this manner in a vacuum tube the successive terms of a fractionation, the spectra observed have nearly the sensibility of other spectra, and the agreement of the different spectra (spark, absorption, phosphorescence) which belong to the same element appears clearly if the treatment has been pushed sufficiently far.

It is not the same thing if we observe the phosphorescence which the earths give directly without addition of lime or other diluent earth, or if only insufficient quantities of diluents are added. Certain earths, such as *gadolinia* or *yttria*, then necessarily play the parts of diluents, and we no longer can observe the concordance of the absorption or spark spectra with the spectra of phosphorescence.

The earths which in my treatments are comprised between gadolinium and yttrium are not directly phosphorescent. They contain terbium, dysprosium, and neo-holmium. Hitherto I have not observed any phosphorescence attributable to the latter element.

By diluting the various terms of my fractionations in lime, I have observed only two phosphorescence spectra, the first belonging to terbium, the second to dysprosium.

Spectrum of Terbium.

633	Nebulous, strong.
630	Weak, connected with the following.
627·5	Rather strong.
625 to 622	Nebulous, connected with the following; strong maximum at 624.
619	Moderate, wide.
601·7	Strong, sharp.
598·7	Moderate.
595·5	Strong.
589·7	Tolerably strong, sharp.
587·8	Strong. (Must not be confounded with the moderate and very hazy line of dysprosium which coincides with it in the mixtures).
584·3	Strong, sharp, and a little more refrangible than the citron band 584·8, with which it is identical in dysprosiferous products.
581·7	Weak, a little more refrangible than the band 583·2, with which it is united in dysprosiferous products.
578·9	Very weak.
568·7 to 560·2	Very diffuse, unsymmetrical band, approximate maximum at 566.
558·8	Moderate, rather sharp.
557·0	Middle of a moderate wide band, connected with the following.
555·0	Very strong, nebulous.
552·1	Very strong, nebulous.
550·8	Feeble.
549·5	Very strong, nebulous.
545·8	Weak, very hazy.
543·8	Strong, hazy, connected with the following.
542·5	Very strong, nebulous.

540 and 539	Maxima of a moderate, nebulous band.
534 to 522·5	Nebulous, weak, and unsymmetrical band, with a maximum at 532·3.
503	Weak, nebulous.
494·5	Weak, very nebulous.
489·5	Moderate, diffuse, connected with the following.
485·5	Very strong and sharp.
482·5	Moderate, diffuse, connected with the preceding one.
478·5 to 473	Weak, very diffused band.
467	Weak, nebulous.
464	Very weak and diffused.
462 to 457	Moderate, very diffused band.
447·2	Rather strong and sharp.
445·5	Rather strong and sharp.
444	Moderate, nebulous.
441	Moderate, nebulous.
439·5	Strong and sharp.
437	Very strong and nebulous.
435	Strong and sharp.
434	Weak, diffused, connected with the preceding.
430	Very weak, diffused.
428	Weak, very diffused.
424·5	Very weak and diffused.
422	Moderate, sharp.
420	Very strong, rather sharp.
419	Strong, rather sharp.
418	Strong, rather sharp.
416	Rather strong, nebulous.
414·5	Moderate, sharp.
414	Rather strong, sharp.
413	Rather strong, sharp.
412	Rather strong, sharp.
391·5	Weak, diffused.
390	Very strong, nebulous.
388	Strong, diffused.
386·5 to 384	Moderate, very diffused.
382	Rather strong, nebulous.
380·5	Strong, nebulous.
379·5 to 378	Very strong, probably double.
377	Strong, nebulous.
375	Weak, nebulous.
373·5	Weak, nebulous.
372	Very weak, nebulous.

Spectrum of Dysprosium.

675	Approximate centre of a strong, rather sharp band.
667	Very weak, diffused.
654·5	Hardly visible.
598·5 to 595	Rather strong, very diffused band, maximum at 595·8.
587·7	Moderate, very nebulous band, which must not be confounded with the strong and sharper band of the same wavelength of terbium.
584·8	Extremely strong and sharp. This is the citron band (Gδ) of Sir William Crookes.*
583·2	Rather strong.
580·5	Moderate.
578·5 and 577·5	Doublet of moderate intensity.
576·3 and 575·2	Doublet of moderate intensity.
573·5	Weak, very diffused.
570·8	Rather strong.
569	Weak, very diffused.
566 to 563·5	Weak band, approximate maximum at 563·4.
506·3 to 500	Weak, extremely diffuse band.
495·5 to 491	Moderate, very diffused. Approximate maximum at 493·5.
490 to 488·2	Strong, diffused.

* *Comptes Rendus*, vol. cxliii., p. 229, July 23, 1906.

* M. Urbain is in error. The wave-length of my citron band is 574 (*Phil. Trans.*, May 31, 1883, Part 3, p. 891).—W. C.

486 to 482.5	Weak band. Maximum at 484.5.
481.5	Moderate, nebulous.
479.7	Strong, nebulous.
477	Weak.
474.8	Moderate, nebulous.
472.8	Moderate, nebulous.
469 to 466.5	Moderate, very diffused.
451	Moderate, diffused.

I may remark that Sir William Crookes attributes the citron band sometimes to an element, Gd, sometimes to yttrium.* Long ago, M. Lecoq de Boisbaudran identified the element producing the citron band with his element Zr. I have shown that the element Zr is identical with dysprosium. To the fact that pure yttria does not give the citron band (Lecoq de Boisbaudran, *Comptes Rendus*, 1866, vol. ciii., p. 113), I will add that the earths I have used to determine the preceding spectra contain no trace of yttrium detectable by the spark or the arc, and we know how great is the sensitiveness of the spectrum of the yttrium lines.

THE DIRECT ESTIMATION OF NITRO - GLYCERIN IN CORDITE, &c.

By OSWALD SILBERRAD, Ph.D.,
HENRY ABLETT PHILLIPS, and HENRY JOHN MERRIMAN.

No method has hitherto been devised for the direct estimation of nitro-glycerin in cordites and allied explosives. It is customary to extract the nitro-glycerin and mineral jelly with ether, and to weigh the residual nitro-cellulose. Methyl alcohol is used to separate the nitro-glycerin and mineral jelly; the latter being weighed and the former determined by difference. The disadvantages of having no direct method for the estimation of such an important constituent of cordite as nitro-glycerin are manifest.

Firstly, the methods for the determination of mineral jelly are somewhat unsatisfactory. Thus, on keeping a powder, a certain portion of the mineral jelly becomes soluble in methyl alcohol, and is therefore estimated as nitro-glycerin; and, secondly, it not infrequently occurs that the powder contains some additional ingredient, the presence of which precludes the estimation of nitro-glycerin by difference.

The chief difficulties met with in attempting to estimate nitro-glycerin in cordite directly are due to the unavoidable presence of a volatile solvent used for its separation. Such solvents interfere with the reactions of nitro-glycerin to such an extent that all previous attempts to devise quantitative methods have been fruitless.

The present method is based on the reduction of the saponification products of nitro-glycerin to ammonia, and will be found to be satisfactory and accurate.

Saponification alone does not give quantitative results. In this connection, Hay's work should be referred to (*Monit. Scient.*, [3], xv., 424). According to this author, the saponification may be represented by the following equation:—



The present work has shown, however, that the reaction is not quantitative, ammonia and other products always being simultaneously formed.

Experimental.

Direct Evaporation of Ethereal Solution of Nitro-glycerin.—A series of experiments in this direction showed—

* This statement is scarcely accurate. I have always ascribed the citron band (λ 574) to yttrium. But having been led, by the results of long-continued fractionation, to the hypothesis that what we now call yttrium may be a mixture of closely allied bodies one only of which is responsible for the citron band, I have called this hypothetical component of yttrium Gd (*Proc. Roy. Soc.*, 1886, vol. xl., p. 506).—W. C.

- That ether cannot be removed from nitro-glycerin without loss of the latter;
- That the loss is reduced to a minimum when the removal of the ether is carried out at a low temperature in a current of air;
- That even under the most carefully controlled conditions constant results cannot be obtained.

As an example, the following experiment may be cited:—Weighed quantities of nitro-glycerin were dissolved in ether, the ether evaporated in a current of air, and the nitrogen estimated by Lunge's method in the residue.

0.4508 grm. of nitro-glycerin originally taken gave 140.8 c.c. of nitric oxide at 758.9 m.m. and 19° C. (= 18.24 per cent N).

0.4501 grm. of nitro-glycerin originally taken gave 140.5 c.c. of nitric oxide at 762.2 m.m. and 22.8° C. (= 18.07 per cent N).

This corresponds to 98.58 and 97.69 per cent of nitro-glycerin respectively. Experiments were therefore carried out with a view to devising a direct method for estimating nitro-glycerin in an ethereal solution. The results which ultimately led to the development of a satisfactory method are briefly summarised in Table I. From these results it will be seen that it is possible to overcome the difficulties attending the direct estimation of nitro-glycerin in ethereal solution (as obtained in the analysis of cordite) by reducing the saponification products with zinc, iron, and caustic soda. Under these conditions the nitrogen is quantitatively converted into ammonia.

The apparatus* consists of a flask fitted with a Soxhlet extractor, which is also fitted with a very efficient condenser, the whole apparatus being joined together with ground-glass joints. These precautions are necessary in order to avoid loss of nitro-glycerin, which is readily carried away in the ether vapour.

The direct estimation of nitro-glycerin in a cordite is carried out as follows:—

A weighed quantity of the ground cordite, sufficient to yield about 2 grms. of nitro-glycerin, is placed in a thimble in the Soxhlet extractor, 80 c.c. of absolute ether is poured into the flask, and extraction carried out in the usual manner. After the extraction of the cordite is complete, the thimble containing the residual nitro-cellulose is washed with a little fresh ether and removed from the extractor. Two absorption flasks, containing 10 c.c. of N/10 acid, are now affixed to the top of the condenser and excess of sodium ethylate (about 50 c.c. of a solution prepared by dissolving 5 grms. of sodium in 100 c.c. of absolute alcohol) run into the flask little by little by means of a side tube. The reaction takes place rapidly, and is completed by warming on the water-bath for about six hours; its course may be followed by periodically drawing off small samples by means of a tap in the Soxhlet extractor and examining them for nitro-glycerin by means of diphenylamine in sulphuric acid. The ether is then distilled up into the Soxhlet and run off by means of tap, the residue is dissolved in water and made up to 250 c.c., the aqueous Soxhlet and ether washings being also added to the solution.

Fifty c.c. of the solution are transferred to the flask of the reduction apparatus, which consists of a flask fitted with a splash head to which is attached a reflux condenser, absorption flasks containing N/10 acid being attached to the condenser. 50 grms. of a mixture of powdered zinc (2 parts) and reduced iron (1 part) are added, together with 50 c.c. of 40 per cent caustic soda solution, and the ammonia distilled off in a slow current of air and collected in standard acid (about 75 c.c. N/10 acid) in the absorption flasks. The excess of acid is then titrated back. 1 c.c. of N/10 acid corresponds to 0.00757 grm. of nitro-glycerin.

The examples given in Table II., which show the nitrogen present as nitro-glycerin, will serve to illustrate the degree

* To be obtained of Messrs. Townson and Mercer, 34, Camomile Street, E.C., or Messrs. Muller, 6, Orange Street, Red Lion Square

TABLE I.—Experiments on the Quantitative Estimation of Nitro-glycerin in Ethereal Solution.

Conditions of experiment.	Percentage of the nitro-glycerin taken found by experiment.	Molecular proportion of reagent per molecule of nitro-glycerin taken.	Remarks.
I. Saponification by boiling the ethereal solution with alcoholic caustic soda.			
1. Product titrated unfiltered..	86.35 (a)	4.32 NaOH	The reaction was hardly complete after twenty-four hours' boiling (b). Ammonia was evolved, and in three cases estimated :— (1) 1.39 } Per cent of the total (2) 1.65 } nitrogen present was (3) 2.09 } evolved as ammonia.
2. " " " " " "	86.48 (a)	4.32 NaOH	
3. Product filtered	88.46 (a)	4.42 NaOH	
4. " " " " " "	89.10 (a)	4.45 NaOH	
II. Saponification by boiling the ethereal solution with alcoholic caustic potash for twenty-eight hours.			
1. Product titrated unfiltered..	84.65 (a)	4.23 KOH	
2. " " " " " "	85.10 (a)	4.25 KOH	
III. Saponification by heating the ethereal solution with alcoholic caustic potash in a sealed tube.			
1. For six hours at 100° C. ..	81.75 (a)	4.09 KOH	
IV. Saponification by warming the ethereal solution with sodium ethylate.			
1.	86.16 (a)	4.31 C ₂ H ₅ ONa	The reaction proceeds much more readily than in the above cases, being fully completed in six hours. Ammonia was evolved and estimated in two cases :— (1) 1.05 } Per cent of the total (2) 0.61 } nitrogen present was evolved as ammonia.
2.	86.53 (a)	4.33 C ₂ H ₅ ONa	
V. Saponified by heating the ethereal solution with alcoholic ammonia in a sealed tube.			
1. For six hours to 100° C. ..	—	1.88 NH ₃	The reaction is obviously incomplete, as at least three molecules of ammonia must be required.
VI. Reduction of ethereal solution to ammonia by means of a copper-zinc couple.			
1. In alkaline solution	69.51	—	Traces of unchanged nitro-glycerin could still be detected in the flask after prolonged boiling.
2. In acid solution	54.26	—	
VII. Reduction of ethereal solution to ammonia with zinc-dust and sulphuric acid in presence of salicylic acid.			
1.	—	—	Reaction violent and altogether unsuited for quantitative work. Results are therefore not included.
2.	—	—	
VIII. Reduction to ammonia by boiling ethereal solution with tin and hydrochloric acid.			
1.	66.39	—	Reduction was carried on for three hours.
IX. Reduction to ammonia by heating ethereal solution with stannous chloride and hydrochloric acid; excess of stannous chloride estimated by titration with one-tenth normal iodine solution.			
1. At boiling-point of ethereal	—	5.63 SnCl ₂	In all cases the quantity of stannous chloride used is insufficient to account for the reduction of all the nitro-glycerin present.
2. solution.. .. .	—	6.40 SnCl ₂	
3. For six hours at 100° in	—	9.76 SnCl ₂	
4. sealed tube	88.35	9.76 SnCl ₂	
5.	81.49	9.66 SnCl ₂	

(a) These figures are calculated on the generally accepted equation for the saponification of nitro-glycerin, according to which one molecule of this substance requires five molecules of alkali.

(b) In aqueous solution the saponification is far slower and less complete, whilst the presence of alcohol prohibits the use of hydrogen peroxide. The method recently published for the estimation of nitrogen in nitro-cellulose (M. Busch, *Ber.*, 1906, xxxix., 1401) is therefore not applicable.

TABLE I. (continued).

Conditions of experiment.	Percentage of the nitro-glycerin taken found by experiment.	Molecular proportion of reagent per molecule of nitro-glycerin taken.	Remarks.
X. Reduction of ethereal solution to nitric oxide by boiling with ferrous sulphate and sulphuric acid.			The nitric oxide was mixed with excess of air, the nitric peroxide produced collected in standard caustic soda solution, and the excess of alkali titrated with N/10 acid. It was found impossible to bring about the completion of the reaction even after prolonged boiling, whilst unchanged nitro-glycerin invariably found its way into the absorption flask.
1.	31.60	—	
XI. Estimation of nitro-glycerin as ammonia produced by the reduction of its saponification products with zinc, iron, and caustic soda.			Calculated to nitrogen, this is—
1.	100.18	—	18.53 per cent.
2.	99.43	—	18.39 " They require 18.50.
3.	99.78	—	18.46 "

TABLE II.

Explosive.	Nitrogen determinations by Dumas' method.			Nitrogen present as nitro-glycerin.	
	Nitrogen in original cordite, &c.	Nitrogen in extracted nitro-cellulose.	Percentage of nitro-cellulose.	Calculated from results by Dumas' method.	Found by new method.
Experimental cordite, F. 140 ..	14.77	12.82	36.33	10.11	10.02
Experimental cordite, 4296 ..	15.53	13.22	31.83	11.32	11.35
Experimental cordite, 2614 ..	13.90	12.85	65.43	5.49	5.47
Blasting gelatin	17.21	11.81	8.26	16.24	16.00

of accuracy of the method. Nitrogen estimations were also carried out by Dumas' ultimate method on the original explosive, and also on the nitro-cellulose separated by ether extraction, and the nitrogen present as nitro-glycerin, calculated from these data, is given for comparison.

The slight discrepancy between the two results when applied to blasting jelly is due to the fact that Dumas' method invariably gives high results when applied to this explosive; the new method is evidently accurate in this case also.

Our thanks are due to the Director of Artillery and the Explosives Committee for permission to publish these results.

Research Laboratories, Royal Arsenal, Woolwich.

ABSTRACT JOURNAL.

WE have received the following communication from Dr. WILLIAM A. NOYES, Secretary of the American Chemical Society:—

Last year the question of raising the dues of the American Chemical Society to eight dollars for the purpose of publishing an Abstract Journal, in co-operation with the Society of Chemical Industry and the London Chemical Society, in case such co-operation could be secured, was submitted to a vote of the members of the American Chemical Society. About 85 per cent of those voting expressed their willingness to increase the dues for this purpose.

A conference with members of the Society of Chemical Industry and of the London Chemical Society was held in the rooms of the latter Society at Burlington House, London, on Friday, July 14, 1905. There were present: Dr. E. Divers, Mr. Watson Smith, and Dr. L. W. Thorne, representing the Society of Chemical Industry, and Prof.

Raphael Meldola, Prof. W. A. Tilden, Dr. Alexander Scott, Prof. M. O. Forster, Prof. Sir William Ramsay, Mr. A. J. Greenaway, and Prof. H. E. Armstrong, representing the London Chemical Society. Dr. Hugh Marshall came from Edinburgh in place of Dr. Leonard Dobbin, a member of our committee who could not be present. The editor of our Journal, Dr. W. A. Noyes, presented the matter for the American Chemical Society. In the discussion which followed representatives of the Society of Chemical Industry expressed the opinion that the difficulties in the way of co-operation were too great. Prof. Ramsay and Prof. Armstrong spoke in favour of co-operation, while Prof. Tilden and Dr. Scott feared that joint publication of abstracts would result in loss of membership to the London Chemical Society. In general, those present seemed to agree that co-operation is very desirable, but the difficulties appeared to the majority as almost insuperable.

After further very careful study of the problems, I submitted to the three societies a plan for co-operation in which it was proposed that each society should prepare abstracts essentially as at present, eliminating duplication of abstracts and collecting all of the abstracts prepared by each society for publication in a single journal. A careful estimate was made of the cost of such a publication and the statistics of membership were carefully gathered. It was shown that about 80 per cent of the individuals belonging to the three societies receive at present only one of the Journals. It was shown, further, that by increasing our dues to eight dollars and increasing the dues of the Society of Chemical Industry to thirty shillings, instead of twenty-five, it would be possible to furnish an Abstract Journal which would combine all that is of value now published by the three societies, into a single Journal, and send this to every member of each society. In reply to this proposition the Society of Chemical Industry decided that it could not take part in such a co-operation. A similar co-operation between our Society and the London Chemical Society seems impossible for the reason that that society is

unwilling to publish abstracts in technical chemistry. An attempt to secure an exchange of abstracts between our own Society and the London Chemical Society on some equitable financial basis has also failed.

In consideration of the desire for a complete Abstract Journal expressed by so many of our members, it seems right for us now to consider the feasibility of publishing such a Journal for ourselves. It is evidently impossible for us to publish at once as complete a Journal as might have been published by co-operation between the three societies. It is estimated, however, that if we increase the dues to eight dollars, and there is no loss in membership, it will be possible to publish twice a month an abstract Journal of from 75 to 90 pages in each number, these pages to contain printed matter $11\frac{1}{2}$ by $18\frac{1}{4}$ c.m., set in eight point type. This would contain an amount of material corresponding to about three thousand pages annually of our present Review of American Chemical Research, and would be a larger amount of material than is furnished in the way of abstracts by either the Society of Chemical Industry or the London Chemical Society.

In this Journal it is proposed to include, as far as possible, abstracts of all important articles upon chemistry published in the world. In order to bring the material within the space prescribed it will be necessary to make the abstracts in organic and physical chemistry very brief, while it is proposed to give somewhat fuller abstracts in other fields, especially in analytical chemistry and in articles pertaining to industrial processes. If it proves possible to maintain the Society at its present membership and rate of increase, it is believed that in a comparatively few years we can increase the length of abstracts in those fields where at first they are especially abbreviated and furnish an Abstract Journal which will be satisfactory to all classes of chemists.

It is proposed to issue the first number of the Journal on January 1, 1907.

In order to undertake the publication of the new Journal it will be necessary to make two changes in the constitution of our Society and two changes in the by-laws. These changes were proposed at the Ithaca meeting, referred to a committee of the Society composed of Drs. J. H. Long, William McMurtrie, and W. A. Noyes, and on approval by the committee were approved by the Council and referred to the Society with the recommendation that the changes be adopted. Please vote on these amendments by means of the postal card which is enclosed.

In case the Society approves of the publication of the new Journal, and votes to increase the dues for this purpose, the hearty co-operation of all our members in an endeavour to prevent the loss of members because of the increase of dues and in the endeavour to secure new members, will be very important. The undertaking which lies before us is a large one and we believe one which is of very great importance not only to ourselves and to the English-speaking chemists of the world, but also to the growth of the science of chemistry.

It is most earnestly desired that every member of the Society shall vote on this question.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 2, July 9, 1906.

Chlorides and Sulphates of Rubidium and Cæsium.—M. de Forcrand.—The author investigates the thermochemistry of the chlorides and sulphates of rubidium and cæsium.

Secondary Alcohols of Dichotomic Octane, $(H_3C)_2-CH-(CH_2)_4-CH_3$.—Louis Henry.—The re-

placing of hydrogen by OH in the CH_2 of the normal carbon chains, $CH_3-(CH_2)_n-CH_3$, has only a very slight influence on the volatility of the corresponding secondary alcohols. The author finds that the boiling-points of these alcohols rise in proportion as their component $-CH(OH)$ is further removed in the molecule from the dichotomic radicle, $\begin{matrix} H_3C \\ | \\ H_3C-CH \end{matrix}$.

Action of the Electric Current on Cyanogen.—H. Gaudechon.—When an electric current acts on perfectly pure dry cyanogen, a body is formed which does not result from the products of the simple polymerisation of cyanogen, but from the solid and soluble products of condensation (rich in carbon) formed during the simultaneous elimination of nitrogen gas. The composition of this product varies with the pressure of the gas, electric capacity of the apparatus, &c. The author describes his apparatus, and finds that the resulting brown body is partially soluble in water and alcohol and totally soluble in dilute alkaline solutions, showing that it cannot contain any free carbon.

Decomposition of Acid Amido-derivatives of Albumins.—Albert Morel.—By introducing, either together or separately, leucine and tyrosine into the molecule of urea the author prepares the following substituted ureas of glycoll:—(1) Isocyanate of ethyl glycoll, $CONCH_2.COOC_2H_5$; (2) urea of glycoll or carbamido-acetic acid, $CO<\begin{matrix} NH.CH_2.COOH \\ NH.CH_2.COOH \end{matrix}$; (3) mixed urea of glycoll and leucine, $CO<\begin{matrix} NH.CH_2.COOH \\ NH.CH.CH_2.CH<\begin{matrix} CH_3 \\ CH_3 \end{matrix} \end{matrix}$; (4) mixed urea of glycoll and tyrosine, $CO<\begin{matrix} NH.CH_2.COOH \\ NH.CH.CH_2.C_6H_4.OH \end{matrix}$. He also investigates the

action of digestive ferments, such as pepsine and pancreatic juice, on ureas and amido-acids.

Condensations with Anthranol.—R. Padova.—The author succeeds in obtaining in the anthracene series a body, corresponding to the diphenylquinomethane of Bisztrizky and Herbst in the benzenic series, which he designates diphenylanthraquinonemethane or diphenylmethyleneanthraquinone.

Reduction of Non-saturated Primary Alcohols of the Fatty Series by Ammonium Metals.—E. Chablay.—The author's experiments show that the ammonium metals can give with non-saturated alcohols interesting reduction reactions, the hydroxyl (OH) being replaced by an atom of hydrogen. He also examines a certain number of these reactions on other non-saturated alcohols of the fatty and aromatic series. The hydrogenation is due to the formation of an alcoholate, the alkaline metal only taking part in the reaction, and there being no transformation into amide as in the case of the halogen derivatives of the carbides. This fact also led the author to study the action of the alkaline metals on alcohols, and he finds that the same reactions take place, but with less intensity. Thus allylic alcohol, when treated with sodium, gives a mixture of hydrogen and propylene, whilst sod-ammonium only gives propylene.

Transformation of certain Secondary and Tertiary α -Glycols into Ketones, and Transposition of Hydrobenzoin.—MM. Tiffeneau and Dorlencourt.—In order that the transformations of bi-secondary or secondary-tertiary α -glycols into acetones shall be accompanied by molecular migrations, it is not enough that the intermediate alcohol formed possess an aromatic radical attached to its oxyhydride, but it is also necessary that the transitory alcohol function is not a vinylic function, as in compounds of the form $ArC(OH)=CRR'$. The transposition of hydrobenzoin approaches in a general manner that of the aromatic iodoaldehydes, but it constitutes an isolated case amongst the glycols.

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THE EVOLUTION OF THE ELEMENTS.*

By F. SODDY.

THE subject chosen for the discussion which I have been asked to open is almost as old as any in philosophy, but the profound change which it has undergone in the last decade makes it desirable to pause, and, looking backward, to review the standpoint that has been attained. I shall attempt to deal briefly with the historical aspect, in the hope of showing how perfectly the newer ideas dovetail into, and arise naturally out of, the hardly-won articles of scientific belief of a generation ago. The new emphatically does not in any sense subvert the old, but the horizon has greatly extended—how greatly is perhaps hardly yet fully admitted. Facts always remain in modern science, and theories, too, in so far as they mirror them completely. So the old facts about the atom and element remain; but the theories, which are the generalised expression of all the facts, have had—in connection with the discovery of radioactivity—to accommodate some new facts of a strange, not to say revolutionary, character. The extension of the theories which have been rendered necessary has not been revolutionary in any distinctive sense. It is wonderful how accommodating a true theory is to new truth apparently of a diametrically opposite character; and this, not in any sense of mere ingenuity of explanation, but in a manner that arrests the investigator, and is his sign that he is on safe ground. From the very first the best proof of the newer views, to my mind, was in the completeness with which the strange newly-won knowledge harmonised with the old, and gave to it a still deeper meaning.

I intend first to consider the distinguishing features of the newer conception of the evolution of the elements, and how it came about that they remained so long unanticipated either in imagination or discovery. Then the new light that has been shed on some of the oldest problems in the more speculative departments of knowledge must be touched on, and this leads naturally to the question as to what are the limitations of the present position. How far does the new view fail to reveal types of evolution which now may be legitimately imagined to be taking place, and of which the only thing we are certain of is that our present weapons are unequal to the task either of discovering or investigating them? Again we have to take in account the poverty of the unaided human imagination and the wealth of suggestion that one fundamentally new point of view awakens. From this point of view it is the advance made that points to an extension of possibilities so great as almost to amount to a revolution of thought; possibilities of the ultimate convergence of these newly-discovered processes and activities of matter on the practical problems of life and the future welfare of the race, which, considered in the light of the known effect of the relatively insignificant forces which have already been harnessed and are taking every day a larger place in our lives, lose none of their suggestiveness for being so vague and incalculable; possibilities of a new order of things—a more extended and exalted material destiny than any that have before transpired, even as possibilities must affect the imagination and lay hold on the thought of the future, none the less even if they continue to remain out of reach. It is in this sense that the new discoveries must affect in time the whole trend of philosophic thought. We are now, however, more nearly concerned with the lines of attack at our disposal for dealing with the new situation which has

presented itself, and in which it must be confessed we feel unusually ill-equipped. The weapons available are rather limited in their range, and there is the possibility that the radio-elements may remain for long the only example of a process of evolution which we cannot but believe will ultimately embrace all the elements within its scope, and lead to a consistent theory of the whole material universe.

More than fifteen hundred years ago, as M. Berthelot has pointed out, the symbol by which matter was everywhere expressed was a serpent, the body coiled into a circle and the head devouring the tail, bearing the central motto "*ἐν το πᾶν*." This was derived from the Greeks, who, in imagination untrammelled by knowledge, far surpassed even the most advanced theory of to-day, supposing that material evolution proceeded in a cycle, and thus were able to arrive intuitively at a system at once continuous, consistent, and eternal, avoiding the inherent difficulties connected with the beginning and end of the process which trouble us to-day. From that time till quite recently, although the idea of continuous evolution of matter was never absent, experimental knowledge advanced steadily along lines which seemed almost to disprove the possibility of any such process. We had Boyle's recognition of an element as a substance which could not be fundamentally changed or made to yield anything more simple, and the continued existence of a relatively few constituent elements throughout all chemical changes. The Law of Multiple Proportions and Dalton's Atomic Theory led to the idea of atoms in their modern experimental sense as the units of all chemical changes—the bricks, so to speak, out of which all molecules are built and into which they can be resolved. The advent of the spectroscope, and the evidence afforded by such meteorites as make their way to us from distant regions, proved the essential uniformity of material composition of the whole universe.

Intimately connected with these researches, another idea took shape as chemistry advanced. Not the slightest variation in the properties of elements could be detected, and hence each atom of any one element must be exactly like every other. It had constants, such as the atomic mass, which is in itself a theoretical abstraction from the experimental combining or equivalent weight, and periods represented by the characteristic lines in its spectrum, capable of being measured with extreme accuracy, and in which the slightest variation in value had never been detected. An atom of hydrogen executes its vibrations by which we know it at precisely the same rate in the most distant star as in the laboratory. This seemed to exclude the possibility of a gradual change or evolution of one element into another. The position cannot be more forcibly expressed than in the familiar words of Clerk Maxwell to this Association at the Bradford meeting in 1873:—

"In the heavens we discover by their light, and by their light alone, stars so distant from each other that no material thing can ever have passed between them, and yet this light tells us also that each of them is built up of atoms* of the same kind as those we find on earth.

"Each atom, therefore, throughout the universe bears impressed upon it the stamp of a metric system as distinctly as does the metre of the Archives of Paris or the double royal cubit of the temple of Karnac. No theory of evolution can be formed to account for the similarity of atoms, for evolution necessarily implies continuous change, and the atom is incapable of growth or decay, of generation or destruction.

"On the other hand, the exact equality of each atom gives to it, as Sir John Herschel has well said, the essential character of a manufactured article, and precludes the idea of its being eternal and self-existent."

In this quotation we have the best generalised expression of the philosophy of a generation ago. To-day we

* A Paper read before the British Association (Section A), York Meeting, 1906.

* I have replaced the word "molecule" throughout by "atom," so as to retain the same meaning for the word atom as it bears throughout the paper.

could deduce even more striking examples of the exact similarity of atoms than were then known, and yet we believe in evolution as an experimentally demonstrated fact.

A little later the swing of the pendulum was again towards some system of evolution. The discovery of the Periodic Law, and the natural order into which the elements fell when classed according to their atomic weight, the recurrence periodically of elements resembling each other in properties, these resemblances extending even to similarity of spectrum, together with the growing knowledge of all that the spectrum of an element implied, led to the view that similar elements must possess similar structures in which the constituent stuff out of which they are built is the same, but the quantity and arrangement different in the formation of each atom. The idea was expressed by the lemniscate curve of Sir William Crookes, that the elements were successively formed out of the same protyle, while in their formation a periodic change of the conditions conditioned the periodic recurrence of properties. A little later Sir Norman Lockyer propounded a theory of inorganic evolution accompanying the cosmical evolution, in which in the hottest stars it was concluded the conditions are such that only the lighter elements can exist, and then as the star cools the heavier elements successively make their appearance by the condensation of the lighter.

Finally we have the brilliant series of researches emanating from the Cavendish Laboratory under J. J. Thomson, in which he succeeded in the isolation and measurement of the constants of the corpuscle or negative electron, and the recognition that this must possess the fundamental attribute of matter, inertia or mass. From this point came the step to the conclusion that negative electricity might be the protyle, out of which all atoms are in some way constructed, by varying numbers being combined together in stable systems in regular motion. But into the more purely speculative part of this theory it is not necessary for me to venture.

I pass to the discovery of the radio-activity of matter by Becquerel and its essential characteristic which at once arrested attention. Here we had a case of certain of the heaviest elements being proved continually to liberate energy of a very novel and striking character, without at first sight any perceptible change in the matter or any exhaustion of the supply. As is well known, this energy is manifested in the emission of new sorts of radiation, and it has been proved that these radiations are in nature much what Newton supposed light to be, consisting of streams of material particles ejected from the matter with hitherto unknown velocities. In general two kinds of radiant particle have been recognised, the α -particle having a mass slightly greater than the hydrogen atom, and the β -particle, which is an electron or corpuscle, many thousand times smaller.

A theory elucidating the mystery was worked out in the laboratories of McGill University, Montreal, under Rutherford, four years ago, and having proved itself adequate to explain the known facts and to suggest innumerable new discoveries, it has received general acceptance. I need only recall the discussion which took place on the subject in this section three years ago, which assisted materially in the favourable reception accorded it, and in this section at least I need only briefly refer to its main outlines.

The atoms, in the case of the radio-active elements, are spontaneously breaking up into atoms of lighter elements, and this change proceeds in each case according to a very simple law. The same definite fraction of the total number of atoms breaks up in the unit of time in the case of any one radio-active element. The α -particle expelled with enormous velocity consists, as we have seen, of an atom a little heavier in mass than the hydrogen atom, and this it seems probable, though it has not been completely proved, is an atom of helium. The residual atom which is left in many cases breaks up again and again, more α or β particles being expelled, the same law as before being followed, only in the succeeding products the fraction

changing in unit time is usually much larger than in the original elements, so that the consequence is that these products have a very limited term of existence, and can only accumulate in minute quantities. The energy that is evolved in this change is so enormous that very slow changes can be observed, where the actual amount changing is so infinitesimal that it is hopeless to attempt to detect it by ordinary methods. This appears at once when it is considered that the smallest quantity of any element that can be detected by the spectroscope contains 10^{10} individual atoms, whereas the disintegration of a single atom accompanied with the expulsion of one α -particle is not greatly, if at all, below the limit of detection by present methods.

At first put forward on radio-active evidence alone, it was not long before additional evidence of the correctness of the view was obtained by the older methods. With the discovery in the laboratories of the University College, London, under Sir William Ramsay, of the production of helium from radium, the fact of the gradual evolution of one element into others passed beyond doubt, and the new methods of investigation received the support of the old in a case where it was found possible to examine the process from both points of view.

The essential features distinguishing the type of evolution revealed by radio-active processes from previous conceptions chiefly claim our attention.

The first consists in the reconciliation of the idea of a gradual evolution of one element from another with the facts of chemistry and spectroscopy which we have seen were at one time interpreted to prove the exact opposite. On the new view the change, though of any degree of slowness so far as the mass of the matter is concerned, is sudden and abrupt for each individual atom. There is no gradual alteration of one element in properties until it changes into another, but an abrupt, or more usually a series of abrupt, step-by-step changes in property accompanying the sudden expulsion of the α -particle. As great a difference exists between radium and its emanation, which is its first product, as between any pair of elements known. Yet it is gradual in the sense that only a small fraction of the total quantity of the radium changes in each unit of time.

Slight as this addition is to make the requirements of chemistry and spectroscopy conform to that of continuous evolution, yet the words of Maxwell clearly show how small a step the most brilliant imagination unaided is able to take. It would be an interesting digression to examine the small part played by the imagination, unaided by existing models or analogies, in mathematical and physical science.

The second distinguishing feature is that the evolution proceeds from the complex to the simple. In all previous ideas a continuous building up of the original protyle into something more and more complex was imagined.

The third difference is that the evolution is actually proceeding under our eyes, instead of having once proceeded in the remote past, or if proceeding now, then only under transcendental conditions impossible to realise in the laboratory, which was the earlier idea.

But the fourth distinguishing feature is the vital one. Hitherto the energy change that must accompany a sub-atomic change had received no consideration, while in the new views it is the dominating aspect. Much takes on a new significance in this light. We have seen how the range of the older weapons of investigation, the balance and the spectroscope, have been left behind. We can understand why it is that these new changes proceed with such complete independence of their environment. All the forms of energy known previously are of such a much lower order of magnitude that it is not to be expected that we should be able to influence the rate of change with the means at our disposal. The explanation is now ready to hand why the elements have hitherto resisted and still resist all attempts to change them. The resistless energy which accompanies the break up of an atom must pre-

exist within the atom and be controlling its history, making it independent of its environment and such forces as we can bring to bear upon it from the outside. For the first time we have a positive proof, if such were needed, of the correctness of the stand taken by chemistry against the claim of the alchemist. There may have existed a lingering doubt in some minds after reading the circumstantial accounts that have been recorded of actual transmutation, that perhaps in some cases the alchemist by chance achieved his ends. Now, however, we know that such could certainly not have been the case on account of the energy which would have been evolved in the change of a heavy element into a lighter one, or absorbed in the reverse process. On the other hand, we can imagine what consequences the successful transmutation of metals would bring in its train, which are not at all those which its devotees have imagined. In this problem our position might be compared to that of the savage who knew something of fire and its possibilities, and yet neither possessed it nor could start or control it. The control and utilisation of fire and other sources of energy means no more to the present than the control and utilisation of the internal energy of matter will mean to the future, if ever it comes to be accomplished.

It is in this aspect also that the most revolutionary changes in previous ideas are rendered necessary. The energy changes accompanying any form of continuous material evolution must be the controlling factor in any cosmical scheme, and the failure to recognise this so deeply affects all the existing views on cosmical and terrestrial evolution that it is difficult to see what will remain when it is rectified. But a beginning has been made, and the discussion that has been arranged in this section must bring forth fruit abundantly. I need only say I would like to see the whole subject reconsidered, now that it is clear that an isolated body in space need not of necessity get cooler although continually losing heat.

There is a small question of nomenclature, the use of the word *atom* now that atoms have been shown to be changeable, which may appear justified if we consider the history of the word. The Greek meaning conveyed by the word was purely an imaginative one, being in fact the smallest particle of matter that can be imagined. From the time of Dalton a new experimental meaning became attached to the word, to signify the smallest part of an element, or the unit, that enters into chemical change, and since chemical changes were the most fundamental then known, the word signified in a derived sense the smallest particle that can exist. To-day the atom still retains the exact meaning it has had for a century, as the unit of chemical change; but chemical change is not now the most fundamental known. Radio-active change is so utterly different that it cannot be considered to have any relation to chemical change.

The view has been expressed to me that since the radio-elements have been shown to undergo changes it is incorrect any longer to speak of their atoms, and the word molecules would meet the case. But this would cause the word *atom* to drop out of scientific use altogether, for no element is safe from the fate which has shown to overtake the radio-elements. On the other hand, if we used the word molecule throughout where now we use atom, and spoke of a molecule of hydrogen where now we mean atom, we should have to revive the old clumsy nomenclature of simple molecules meaning atoms, and compound molecules meaning molecules.

Limitation of Present Methods.—Our knowledge of material evolution has arisen almost entirely on account of the energy emitted in the processes, the material evidence, as in the proof of the production of helium from radium, being of necessity only confined to a few cases. The general condition which determines whether any process of spontaneous evolution comes within our experimental methods of detection is simply that the energy evolved should be sufficient in quantity and suitable in kind. There is no doubt that in the actual case of the radio-

active elements the conditions are exceptionally favourable. Probably in no other branch of physics can such a minute evolution of energy be detected and accurately measured as in radio-activity. The electroscope is the oldest and simplest, as it is the most sensitive electrical instrument, and in proper hands possesses possibilities for accurate measurement by no means to be despised. It may seem to conflict with what has been said as to the enormous quantities of energy liberated during radio-active processes that such delicate methods should be demanded, but that is because the actual amount of matter changing is always infinitesimal, even under the most favourable circumstances.

Since the theory of atomic disintegration was advanced it has become more and more plain that such disintegration may and does occur without the accompaniment of radio-activity. We now rather regard radio-activity as a gratuitous hint given us, one might almost say overlooked, by Nature into secrets we were not bound ever to have known of at all. For the same result and the same type of evolution could have been accomplished and may actually be going on without our possessing any means to discover or investigate it. Three separate lines of evidence which have lately transpired show this in the clearest possible manner. In the first place Rutherford proved the existence of changes in the disintegration series of radium, thorium, and actinium, in which no detectable radiation was expelled. Let A change into B, and B into C, and C into D. The middle change of B into C might be a "rayless" change, but it would still be possible to detect it so long as detectable radiation were expelled from A and C. The same point may be illustrated also by a slightly different case taken from an investigation four years ago in a series where some of the changes only emit α -rays, and others both α and β rays. If some of the radium emanation, which emits α but not β -rays, is put into a vessel with thin walls, capable of absorbing completely the α -radiation and allowing the β -radiation to pass through, no external radiation can be detected from the vessel when the emanation is first introduced. Little by little as the emanation begins to change an external radiation makes its appearance and gradually grows. If now the emanation is blown out of the vessel, the products of its change, being solid, are left behind deposited on the inside walls. The external radiation is not at all affected, but as time goes on gradually decays away. It would not have made any difference to the above experiment if the emanation had not given out rays. Its existence could have been inferred from its producing a body which did give out rays, and moreover the rate of its change into this body could be determined. In this way Rutherford has established that changes occur without the emission of a detectable amount of energy, but which are nevertheless demonstrable because they are preceded and followed by changes in which detectable energy is given out.

In the next place the past two years' work on the nature of the α -ray has shown clearly that it is only detectable within somewhat narrow limits of velocity. If we represent the velocity of the fastest moving α -particle expelled from radium by 100, then it has been shown that an α -particle moving with a velocity below 60 would fail to be detected by all our methods, electrical, photographic, or phosphorescent. The identical α -particle we know, through radio-active tests, might be expelled with a velocity up to 10,000 miles a second, and we should be unaware of it and incapable of detecting it by its energy.

Lastly, the possibility remains to be considered that such a particle might be detectable by its charge. I need only mention the ingenious contrivance of Strutt, popularly known as the radium clock, to illustrate a possible method. This detects the loss by radium of negative electricity carried away by the negatively-charged β -particles. In the same way it might be thought that an otherwise undetectable α -radiation might be detected by the loss of positive electricity. This hope, however, proves illusory.

There are theoretical grounds which made me suspect that the positive charge carried by the α -particle is an accident of the conditions under which it was examined, and that the α -particle is not charged when initially expelled from the atom. This I have now proved to be the case, and so far as we can see, if its energy was below that at which it could be detected, the α -particle never would become charged at all.

So that unless entirely new methods of investigation are discovered, we are forced back in the search for direct evidence of other processes of evolution on the purely material methods, such as the use of the spectroscope. Large quantities of materials are required; these materials are the more likely to be changing the rarer they are, which makes the research very costly, and in the end it is by no means certain that a single lifetime is long enough to give to the investigation to secure a positive result.

A possible research along these lines, which I started a year ago, but have not yet pushed very far owing to lack of time and material, is the examination of old coins, medals, and ornaments of undoubted antiquity, for evidence of occluded helium or similar gases. The age or date of manufacture of such articles can often be accurately fixed by the expert, and there is a tolerable certainty that the metals were melted during manufacture and have not been heated since. It seemed that if helium or other gas were found, a definite idea of the magnitude of the rate of change was arrived at as a preliminary to direct experiments. But a good deal of material is required, which need not necessarily have any great antiquarian value so long as its antiquity is above suspicion. An application for help to the British Museum failed, although individual officials have assisted me in the most generous manner from their own collections. But certainly the line of work looks promising enough to justify an attempt if the requisite quantity of material was forthcoming. In the meantime I have been engaged in a determination of the minimum quantity of helium and argon detectable by the spectroscope, and with some new methods find I can be sure of 1/2000 part of a cubic millimetre. This is by far the smallest quantity of any element that has with certainty been detected with the spectroscope.

Taking the possible methods in order of their directness and certainty, we come next to the method which has already given valuable evidence to prove that radium is being produced from uranium. If two elements can be shown to occur in constant relative quantity together in all cases in nature, this of itself is the strongest indirect evidence that the one is the parent of the other. The relative quantities of all the successive members of a disintegration series present with the parent element, attain with lapse of time a constant equilibrium value when as much of each is being formed as disappears in each unit of time. If the parent element is the longest lived member of the series, the relative amounts of each member, when the equilibrium state is reached, is inversely proportional to the relative rates of change, or directly proportional to the average life of each. Thus the researches of Strutt and Boltwood have proved that the amount of radium in all the natural uranium minerals is proportional to the quantity of uranium. This ratio is roughly one to a million, and represents the ratio of the life of radium to that of uranium.

The importance of this result is that it is not confined to radio-active changes. It is a simple deduction which holds good in any series of successive changes where the first change is the slowest, and each member changes into the next at a rate proportional to its quantity. If the rate of change of any member is rapid, the equilibrium amount that can accumulate is small; if the rate of change is slow, it will be large. Thus polonium, which is formed from radium, has never yet been obtained in quantities greater than the fraction of a milligram, although many tons of pitchblende have been worked up for it. Half of it changes in 143 days, which is more than a thousand times faster than radium. Hence the activity is of the order of

a thousand times greater, but correspondingly the quantity in pitchblende is of the order of a thousand times less than in the case of radium.

No other cases except those mentioned of two elements always occurring together in constant ratio in nature have as yet been proved, but if this is done it is as stated almost sufficient to prove that the rarer element has been formed from the one present in greater abundance, and is itself changing further into some other constituent of the natural mineral.

It remains to point out the limitations of this argument. No equilibrium state can be reached if the parent element is not the most stable of the series. If, for example, thorium were being produced from uranium, there could be no constant ratio between the quantities of uranium and thorium, for the rate of change of the thorium is five times slower than that of uranium, according to a recent accurate determination of Bragg. This limitation serves to show that the case is likely to be rare if the instability of the radio-elements, as is commonly supposed, is in some way connected with their heavy atomic weight.

We are thus led to consider constancy of association in nature apart from a constant ratio of quantity. This it will be remembered gave the necessary clue indicating helium as a disintegration product of radium.

These cases are common enough in chemistry, but little can be at present deduced from present knowledge. Tantalum and niobium are two inseparable companions in nature. Donald Murray has recently directed attention to the companionship of silver and lead in this connection, and examples could be multiplied. We are still in darkness as to whether there is any process complementary to disintegration, simultaneously building up the elements of heavier atomic weight, and maintaining their quantity, and this constant association in nature could result as well from a simultaneous formation of both elements as from the change of one into the other. Without other evidence no certain conclusion can yet be drawn in this field.

A slightly different phase of the same question is seen in an element having an approximate constant rarity in nature after prolonged and extensive search for it, I have drawn attention to the fact that the coinage metals, in particular gold, silver, and platinum, of necessity fulfil this condition more or less completely, indicating that these metals are likely subjects for a direct examination. I have already referred to the case of coins, where a direct examination is probably more likely to yield fruit than in any other case.

So far as the economic evidence goes, the scarcity of gold is a matter of concentration, like that of radium, for in small quantities it is like radium very widely distributed. Seeing that 500 tons of gold were produced last year the element can scarcely be scarce in any other sense of the word. It has the remarkable property of being found just whenever the demand for it increases, and the providential character of this behaviour makes me suspect that a law similar to that regulating the scarcity of radium was in question. If this turns out to be well-founded the theory of currency will be reduced to a branch of physics. We may anticipate a more scientific system of currency being devised than the present, which, in 1904, cost the world from fifty to a hundred million pounds value, thrown away in the unproductive labour of maintaining the gold and silver currency.

So far, only what may be termed passive lines of investigation have been considered where processes of spontaneous evolution are supposed to be taking place. There is no evidence whatever that any of the known processes can be in any way artificially influenced. If such were possible it would be tantamount to an artificial transmutation. But at least we know the lines along which even this more ambitious attempt might have a chance of success. The matter in question should be as minute in quantity and the energy acting upon it as intense as possible. These conditions are realised in the case of the residue of gas left in an X-ray bulb through which large amounts of electrical energy of great intensity are passed. The idea has long

been held that possibly in these bulbs the disappearance of the gas with use, resulting in the gradual improvement of the vacuum so well known to the X-ray operator, may be due to a real transmutation or resolution of the gas under the drastic treatment to which it is exposed. But no experiments have been published so far as I am aware along these lines, and the whole subject has not yet advanced beyond the speculative stage.

It remains to be seen whether the lines of investigation here sketched will bear fruit. With the problem of artificial transmutation is linked that of the ultimate utilisation of the internal energy of matter, the solution of which would alter our whole destiny. Its importance therefore cannot be questioned. But the magnitude of the problem is reflected in the difficulties which beset its investigation, and it may be that the single life of the individual and his limited resources will have to be replaced by an organised assault by institutions provided for the purpose, where continuity of purpose and large scale operations can be secured.

PHOTOGRAPHS OF THIN LIQUID FILMS.*

By HERBERT STANSFIELD.

MR. STANSFIELD, who is continuing in Manchester Professor Reinold and Sir Arthur W. Rücker's work on soap films, showed a number of photographs taken with a special camera which has been previously described (*Proc. Roy. Soc.*, 1906, A, lxxvii., 314). The photographs showed the thinning process of plane vertical soap films; at first, when the film is thick enough to show colours, the thinning takes place continuously, but when the thickness is reduced to about 100 μ ($1 \mu = 10^{-6}$ m.m.) there is a change in the conditions, and further thinning takes place by a series of abrupt steps. Films formed from solutions of sodium or potassium oleate in water pass through three distinct grey stages before they become black; the successive changes in thickness become more marked as the film becomes thinner.

Photographs were also shown of the last stage in the thinning process; the change from the black which is first formed to a thinner black probably only half as thick. Johannot gives the thickness before and after this change as 12 and 6 μ respectively. This phenomenon was observed by Newton, and is rather striking in the case of the sodium oleate films; the change was not so marked in the photographs of potassium oleate films, as some of the material removed in the reduction of thickness was left distributed as small specks in the thinner black.

In conclusion, photographs were exhibited showing effects produced by the separation of solid material in soap films.

NOTE ON ERGOT ALKALOIDS.†

By G. BARGER and F. H. CARR.

THE crystalline alkaloid ergotinine was obtained from ergot by Tanret more than thirty years ago, and does not seem to have been studied chemically since then, no doubt owing to its extreme scarcity. Tanret assigned to ergotinine the formula $C_{35}H_{40}O_6N_4$, based on rather scanty analytical data; the molecular weight was deduced by analysis of the amorphous hydrobromide and hydrochloride of very doubtful purity.

We have been able to confirm Tanret's figures for the percentage of carbon and of hydrogen in ergotinine (roughly C=68.5 per cent, H=6.5 per cent), but find nearly 3 per cent more nitrogen (11.7 instead of 9 per cent).‡

* Abstract of a Paper read before the British Association (Section A), York Meeting, 1906.

† Abstract of a Paper read before the British Association (Section B), York Meeting, 1906.

‡ We used Dumas' method; Tanret worked according to Will and Varrentrapp. We are indebted to Dr. P. Haas for two of the determinations, in which he proved the absence of methane in the residual nitrogen gas.

Molecular weight determination in phenol solution by the cryoscopic method gave the values 477 and 516; in pyridine solution the value 463 was obtained, employing a microscopic vapour pressure method due to one of us (G.B.).

Without as yet definitely assigning a formula to ergotinine we suggest that the alkaloid probably has the composition $C_{28}H_{32}O_4N_4 = 488$.

It will be seen that the ergotinine molecule is not more complex than that of several well-known alkaloids, and that it is smaller than Tanret imagined. It is unique among alkaloids in having four nitrogen atoms.

Like Tanret, we have failed to prepare crystalline salts or other crystalline derivatives of ergotinine.

Ergotinine apparently contains no phenolic hydroxyl and no methoxy-group. It is probable that there is a methyl group attached to one of the nitrogen atoms. In methyl iodide solution a gelatinous methiodide is formed, and when one molecular proportion of bromine is added in chloroform solution, a hydrobromide, probably of monobrom-ergotinine, separates out.

From the ethereal mother-liquors of crystalline ergotinine Tanret obtained another non-crystalline alkaloid, which he termed amorphous ergotinine. A similar resinous substance of alkaloidal nature and great physiological activity was described by Kobert as cornutine.

We have now obtained the second alkaloid in a state of chemical purity, and suggest for it the name *ergotoxine*. Though itself amorphous it forms a number of crystalline salts. The oxalate crystallises from alcohol in minute prisms, mostly arranged in rosettes; the tartrate forms prisms; the phosphate fine needles, frequently grouped in sphaerites.

Unlike ergotinine, ergotoxine readily dissolves in aqueous caustic soda and gives a benzoyl derivative by the Schotten-Baumann method; it probably contains a phenolic hydroxyl.

The analytical data so far obtained point to a formula differing but slightly from that of ergotinine, and as both alkaloids occur in the same plant, it is probable that they are closely related chemically (as are, for instance, quinine and cinchonine).

Both alkaloids give strongly fluorescent solutions, and give with sulphuric acid and ferric chloride the play of colours originally described by Keller as characteristic of ergotinine.

According to the physiological experiments of Mr. H. H. Dale, ergotoxine produces in doses of a few milligrams. all the typical effects of ergot described by him in a recent paper (*Journ. of Physiology*, 1906, xxiv., 163). There seems little doubt that it is the most important, if not the one essential active principle, whereas pure crystalline ergotinine is physiologically almost or quite inactive.

ON THE TEMPERATURE AT WHICH WATER FREEZES IN SEALED TUBES.*

By Prof. H. A. MIERS, F.R.S., and Miss F. ISAAC.

THE authors showed in 1905 that, in a cooling supersaturated solution in which a few crystals are growing while it is being stirred, the refractive index rises until, at a certain temperature, it attains a maximum value and then suddenly falls; at this moment also profuse crystallisation takes place. They concluded that this is the temperature of spontaneous crystallisation. The conclusion is confirmed by the fact that the same solution, enclosed in a sealed tube so as to be preserved from access of crystal germs, and protected from evaporation, crystallises in a shower at exactly this temperature.

The present experiments, 68 in number, were made with water contained in sealed tubes which were violently and

* Abstract of a Paper read before the British Association (Section B), York Meeting, 1906.

continuously shaken by hand in a bath of brine. The temperature of the brine was reduced by means of a tube coil through which the cold brine from a refrigerating machine was pumped; the brine in the bath was kept thoroughly stirred by a wooden horse-shoe shaped plunger perforated with holes. The rate of fall of temperature was about 2° an hour. Temperatures were read by a thermometer divided to one-tenth of a degree.

The water in the tube was either tap-water, or ordinary distilled water, or pure water of conductivity 1.1 ± 10^{-6} , and filled about half the tube.

The initial temperature of the brine bath varied from $+9^{\circ}$ to -2° C.

The time occupied in each experiment varied from seventy minutes to five minutes.

The glass used was both ordinary glass tubing and Jena glass. Some of the tubes were made up just before the experiment; some had been made up weeks before.

All the tubes froze between -2° C. and -1.6° C.; the mean for all the experiments being -1.86° C., and for the pure water -1.9° C.

The ice generally makes its appearance at the bottom of the tube, and grows very rapidly, at first in star-like crystals, and then in a cloudy shower which spreads up through the tube.

The authors conclude that -1.9° C. is the temperature at which, under atmospheric pressure, pure water freezes spontaneously, *i.e.*, in the absence of solid particles of ice.

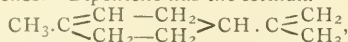
It is remarkable that this is also the temperature at which super-cooled water possesses a maximum refractive index, according to the observations of Pulfrich.

The effect of friction was studied by introducing glass, garnet, galena, or lead into the tubes; this caused the water to freeze at -0.4° C.

NOTE ON THE POLYMERISATION OF ISOPRENE.*

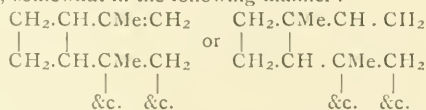
By Prof. W. A. TILDEN.

MANY years ago I showed that the principal terpenes when decomposed by heat yield, among other products, a small quantity of isoprene, C_5H_8 . The constitution of this compound has since been shown by Euler (*Ber.*, 1897, xxx., 1989) to be expressed by the formula $CH_2:CH.CMe:CH_2$. When kept for a long time isoprene is slowly converted into indiarubber, the process, however, occupying many years. The specimens now exhibited illustrate the process of transformation. If any attempt is made to hasten the operation, as by heat or contact with strong reagents, the greater part of the hydrocarbon is converted into dipentene, and the mixture of viscid compounds of high boiling-point, known as colophene, which results from the polymerisation of the terpenes. Dipentene has the formula—



and colophene, no doubt, also contains a number of six-membered rings.

It appears probable, therefore, that the slow polymerisation which ultimately results in the production of solid indiarubber is due to a different mode of linkage, leading to the formation of long chains. Except on the assumption of a shifting of hydrogen this can only take place on condition of the formation of a series of tetramethylene rings, somewhat in the following manner:—



Indiarubber, though of high molecular weight, is an unsaturated substance, as shown by the fact that it absorbs oxygen from the air and unites chemically with sulphur and other elements.

* Abstract of a Paper read before the British Association (Section B), York Meeting, 1906.

THE

STUDY OF HYDRO-AROMATIC SUBSTANCES.*

1. *The supposed Identity of Dihydrolaurelene and Dihydroisolaurelene with 1:1-Dimethylhexahydrobenzene.*—In the last Report (1905, p. 153) brief allusion was made to the preparation of 1:1-dimethylhexahydrobenzene (Crossley and Renouf, *Journ. Chem. Soc.*, 1905, lxxxvii., 1487), and it was stated that the main object in view when preparing this hydrocarbon was a comparison of its properties with those of dihydrolaurelene and dihydroisolaurelene, with which hydrocarbons it has been supposed by Zelinsky and Lepeschkin to be identical (*Annalen*, 1901, cccxix., 303). This comparison has now been completed (Crossley and Renouf, *Journ. Chem. Soc.*, 1906, lxxxix., 26), with results which prove conclusively that neither dihydrolaurelene nor dihydroisolaurelene is identical with 1:1-dimethylhexahydrobenzene, as will be seen from the following summary of their properties:—

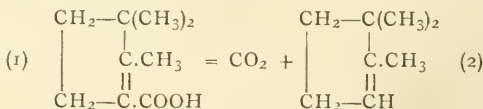
1:1-Dimethylhexahydrobenzene. — Boiling point, 120° ; specific gravity, 0.7864; odour, resembling geranium; oxidation product, 8,8-dimethyladipic acid.

Dihydrolaurelene. — Boiling point, 111.5° — 114° ; specific gravity, 0.7633; odour, camphoraceous; oxidation product, oxalic acid.

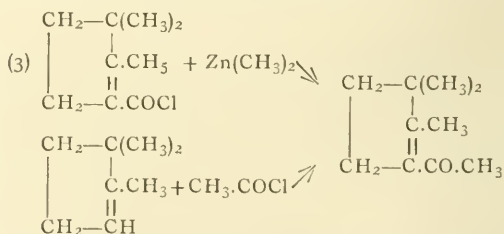
Dihydroisolaurelene. — Boiling point, 113° — 113.5° ; specific gravity, 0.7762; odour, sweet camphoraceous; oxidation product, $\alpha\alpha$ -dimethylglutaric acid.

There is little to be said regarding the constitution of dihydrolaurelene on the present occasion, but it seems most probable that this substance is a mixture of hydrocarbons; whereas dihydroisolaurelene is proved by the following considerations to be a pentamethylene derivative.

In 1898 Blanc definitely established the constitution of isolaurelene in the following manner (*Bull. Soc. Chim.*, 1898, [3], xix., 699). Accepting his formula for isolaurenic acid (1) as correct, he believed isolaurelene to be represented by Formula 2.

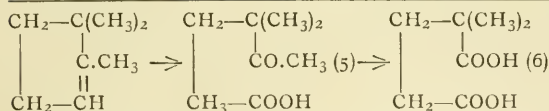


That is to say, that during the loss of carbon dioxide no change in the structure of the ring takes place. This was proved by the fact that isolaurenic chloride (3), when treated with zinc methide, gave rise to the same ketone (4) as is produced by the action of acetyl chloride on isolaurelene in presence of aluminium chloride:—



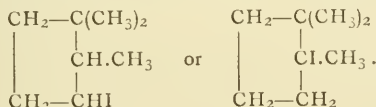
Blanc further showed that when isolaurelene was oxidised with potassium permanganate there was obtained γ -acetyl-dimethylbutyric acid (5), previously obtained by him from the oxidation of isolaurenic acid (*Bull. Soc. Chim.*, 1898, [3], xix., 533).—

* Report of the Committee, consisting of Dr. E. Divers (Chairman), Professor A. W. Crossley (Secretary), Professor W. H. Perkin, Dr. M. O. Forster, and Dr. H. R. Le Sueur. Read before the British Association (Section B), York Meeting, 1906.

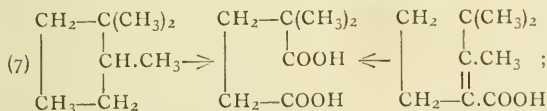


and this ketonic acid, on further oxidation, gave $\alpha\alpha$ -dimethylglutaric acid (6). As Blanc says, the formation of γ -acetyldimethylbutyric acid by the oxidation of isolaurene shows that it can only have the constitution represented by Formula 2, and no other. Yet Zelinsky and Lepeschkin, in 1901, did not accept this conclusion, but regarded isolaurene as a six-ring compound.

Accepting, then, Formula 2 for isolaurene, the next step was to prove that when isolaurene was treated with fuming hydriodic acid at a temperature of $120-125^\circ$ no change in the nature of the ring was produced. For this purpose the hydriodide was treated with diethylaniline, when it readily lost the elements of hydrogen iodide, giving an unsaturated hydrocarbon, C_8H_{14} , boiling at $108-108.5^\circ$, and possessing properties identical with those of isolaurene. In order that there should be no doubt on this point, the hydrocarbon was oxidised with potassium permanganate, when it yielded γ -acetyldimethylbutyric acid, and this, on further oxidation with sodium hypobromite, gave $\alpha\alpha$ -dimethylglutaric acid. These are the same products as Blanc obtained by the oxidation of isolaurene (see above), and conclusively prove that no isomeric change takes place during the production of the hydriodide, which must therefore have one of the following formulae:—



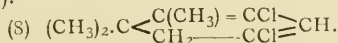
There is, moreover, no reason to suppose that heating this hydriodide with zinc dust in aqueous alcoholic solution would produce a change in the construction of the ring, and this is proved by the fact that when the resulting hydrocarbon (dihydroisolaurene) is oxidised with diluted nitric acid, it gives rise to $\alpha\alpha$ -dimethylglutaric acid:—



that is, to the same oxidation product as isolaurenic acid yields when treated with diluted nitric acid (*Bull. Soc. Chim.*, 1898, [3], xix., 284).

These experiments prove conclusively that dihydroisolaurene is a pentamethylene derivative, and is 1 : 1 : 2-trimethylcyclopentane (7)—a deduction which receives striking confirmation from the magnetic rotation of dihydroisolaurene, which has been determined by Dr. W. H. Perkin, sen.

2. *The Action of Phosphorus Pentachloride on Trimethyldihydroresorcin.*—In the nature of the substances produced, this reaction (Crossley and Hills, *Journ. Chem. Soc.*, 1906, lxxxix.) resembles closely that of phosphorus pentachloride on dimethyldihydroresorcin (Crossley and Le Sueur, *Journ. Chem. Soc.*, 1902, lxxxi., 826, 1533), for two bodies are obtained: one hydroaromatic, namely, 3 : 5-dichloro-1 : 1 : 2-trimethyldihydrobenzene (8); and the other aromatic, namely, 3 : 5-dichloro-1 : 2 : 6-trimethylbenzene (9).



But whereas, in the case of dimethyldihydroresorcin, about 75 per cent of the theoretical yield of the hydroaromatic dichloride is formed and only a very small propor-

tion of the aromatic substance, with trimethyldihydroresorcin the result is reversed, the principal product being dichlorotrimethylbenzene.

Dichlorotrimethyldihydrobenzene can be converted into dichlorotrimethylbenzene under the influence of phosphorus pentachloride or bromine, and it has been ascertained that during this conversion the wandering methyl group passes into an ortho-position, as has already been observed with several derivatives of dimethyldihydroresorcin (*Journ. Chem. Soc.*, 1902, lxxxi., 1534; 1904, lxxxv., 264). This has been proved by analogy, and by a study of the properties of the aromatic dichloride and of the possibility of directly esterifying the dichlorobenzenetricarboxylic acid (dichlorohemimellitic acid) obtained by oxidising dichlorotrimethylbenzene with nitric acid in sealed tubes.

(To be continued).

THE PASSAGE OF ELECTRICITY THROUGH LIQUIDS.*

By W. C. DAMPIER WHETHAM, M.A., F.R.S.,
Fellow of Trinity College, Cambridge.

OUR subject of this evening owes much of its early development to researches carried on in the Royal Institution. Here Davy investigated the chemical effects of electric currents, and, in 1807, discovered the elements potassium and sodium by the decomposition of the alkalis by the electric current. Here Faraday discovered the quantitative relation between the strength of the electric current on the one hand and the amount of chemical action on the other, and thus raised the subject to the rank of an exact science.

Let us pass an electric current through a solution of some salt, and observe the resultant changes. To make these changes visible, let us choose a coloured salt, such as copper sulphate. As soon as the circuit is completed, we see that one of the copper terminals or electrodes, by which connection is made with the solution, begins to dissolve away, while copper is deposited on the other electrode. Thus copper passes through the solution, disappearing at one end and appearing at the other. The direction in which the copper passes is that which is taken conventionally as the direction of the electric current.

It will be seen that the middle part of the solution is unaffected. The chemical changes occur at the electrodes only; at one copper is deposited, at the other copper is dissolved as sulphate, showing the presence of acid in contact with the metal. The chief facts to be explained, then, are the appearance of the opposite constituents of the salt—copper and acid—at the electrodes, and the total absence of change in the body of the solution.

We may explain these phenomena by the supposition that oppositely moving streams of the two parts of the salt proceed through the liquid. In the middle there will always be equal quantities of the opposite parts, and the concentration of the solution is unaltered, but at the ends the parts are set free. The conception may be illustrated by a model, in which differently coloured balls, fixed to movable strings, represent the opposite parts of the salt.

These moving parts of the salt must be electrified, since they move when acted on by an electric force. They were called by Faraday the ions. To a further study of the nature and properties of these ions I ask your attention to-night.

Faraday found that, on passing a steady electric current through a decomposable liquid or electrolyte, the amount of chemical decomposition was proportional to the strength of the electric current, and to the time of current-flow—that is, to the total quantity of electricity which passes. Hence a given quantity of any ion, such as copper or chlorine, must carry with it a definite charge of electricity. Moreover, the mass of substance deposited by a given

* A Discourse delivered at the Royal Institution, February 16, 1906.

current in a given time was found to be proportional to its chemical equivalent weight. Thus equal numbers of equivalents, whether of the same or of different ions, must be associated with equal charges.

If we accept the atomic theory, we must regard the chemical equivalent weight of a substance as proportional to the mass of its atom divided by its valency, *i.e.*, by the number of univalent atoms—such as that of hydrogen—which one atom of the substance will combine with or displace. Faraday's experiments then mean that each univalent ion carries the same charge of electricity, each divalent ion twice that charge, and so on. The charge on one univalent ion is a true natural unit of electricity, which is thus seen to be quite as atomic in its nature as its matter.

We must now regard the process of electrolysis (*i.e.*, the passage of electricity through a decomposable liquid or electrolyte) as a kind of convection, the electric current being carried through the liquid somewhat as water may be carried from point to point in a number of buckets.

If a current be passed for some time through a solution, such as that of copper sulphate, not only is copper dissolved from the anode, or plate by which the current is said conventionally to enter the solution, and deposited at the cathode or place of exit, but a notable change in concentration is noted in the solution near the two electrodes. The liquid near the anode becomes more concentrated, and that near the cathode more dilute. This may easily be illustrated by an experiment. If instead of copper we use platinum as anode, it is not dissolved, and the total amount of copper in solution progressively diminishes. We then find that, while salt is taken from the neighbourhood of both electrodes, more comes from the cathode than from the anode. These phenomena were studied extensively by Hittorf about the years 1850—1860.

Two explanations of this uneven dilution of the solution are possible. We may suppose that the ions are complex structures, and drag unaltered salt or solvent with them through the liquid, or we may suppose that they move with unequal velocities. It is now probable that in some cases both these factors come into play, but, to simplify our ideas, let us first imagine that the opposite ions are simple, or at all events loaded with equal amounts of salt or solvent, and that they move with unequal speeds through the liquid. The use of the model to which we have already referred enables us to see clearly that the velocity of the anion is to that of the cation as the amount of salt lost by the solution near the cathode is to that near the anode. The ratio of the opposite velocities of simple ions could then be deduced from experiment.

In the year 1879, it was pointed out by F. Kohlrausch that the sum of the opposite ionic velocities might be calculated from a knowledge of the electrical conductivity of the liquid. The conductivity, that is the amount of current conveyed under the influence of a given electromotive force, is obviously proportional to the number of ions, to the velocity with which they move, and to the electric charge carried by each. On the assumption that all the salt is actively concerned in conveying the current, we know the number of grm.-equivalents of either ion present from a knowledge of the concentration of the solution. Now Faraday, as we have said, discovered that the amount of substance deposited at the electrodes by a given quantity of electricity was proportional to the chemical equivalent of the substance. This means that a given number of ions, whatever their nature, so long as their chemical valency be the same, carry the same amount of electric charge. The charge on a univalent ion is thus seen to be a true natural unit of electricity; the charge on a divalent ion consists of two such units; that on a trivalent ion, of three. Faraday's quantitative measurements tell us the charge on a grm.-equivalent of any univalent ion. The concentration of our solution tells us the number of grm.-equivalents present; thus, by measuring the conductivity, we can calculate the velocity with which the ions move under a given electric force. By this method,

Kohlrausch calculated the specific velocity of many simple ions when moving through dilute aqueous solutions.

In 1886, Sir Oliver Lodge rendered visible the movement of ions which hitherto had been seen by the eye of faith only. By forcing hydrogen ions from a vessel of acid through a tube containing a jelly solution of sodium chloride, he rendered their presence visible by an indicator which changed colour in the presence of an acid, and thus watched their progress through the tube.

In order to compare the ionic velocities as directly observed with those calculated by Kohlrausch, further modifications of the method are necessary. One arrangement which may be used is to employ two solutions which have a common ion, different densities, a nearly equal specific resistance, and different colours. One of these solutions is placed on the top of the other and a current passed across the junction, the movement of which gives us the velocity of the coloured ions. This method is restricted in scope, but the use of jelly solutions, in which the velocities are not markedly different from those through solutions in water, enables us to use traces of precipitates or indicators to show the movement of various ions. Such experiments showed that the observed velocities were in general agreement with those calculated by Kohlrausch.

If the specific resistances of the two solutions be not equal, interesting phenomena occur at the boundary. The electric force will be greater in the solution where the resistance to be overcome is greater. Hence if an ion from the other solution chance to pass the boundary, it finds itself subjected to a greater force, and its velocity is increased. It will thus be pushed further in advance of the junction if it has got in front, and will be brought up into line again if it has straggled behind. We see, then, that if a junction be advancing in the direction of the solution of higher resistance, the junction will become vague and indistinct, while if the advance be towards the solution of lower resistance the junction will keep sharp and well defined. When the solutions have one ion in common, this means that in order to secure a sharp boundary, we must arrange that a specifically slower ion shall follow a faster one.

Professor Orme Masson recognised that these principles enabled us to dispense with the necessity of choosing two solutions of equal resistance. A salt with quickly-moving ions, such as potassium chloride, is placed in a jelly solution in a horizontal tube. A slow coloured cation is forced electrically into the tube from one end and a slow coloured anion from the other. Thus blue copper may follow the potassium, and the yellow chromic acid ion CrO_4 may follow the chlorine. The higher specific resistance in the two coloured solutions forces their ions to conform to the movement of the potassium and chlorine, and thus the motion of the boundaries gives us the velocities of the potassium and chlorine in a solution of constant and known concentration, and therefore their velocities under a known electric force.

Further improvements were made by Mr. B. D. Steele and Mr. F. B. Denison. The use of jelly in the tube was dispensed with by placing membranes over the ends of the tube, and removing them when once the junctions had got well within it. The use of coloured solutions also was found to be unnecessary, for, with sharp junctions, the line of demarcation was visible, owing to the slight difference in the refractive indices of the solutions, and may be shown by projection on a lantern-screen. Denison and Steele have made a careful series of experiments by this method, and in their hands it is probable that the results thus obtained are more accurate than those given by the methods of Hittorf and Kohlrausch.

The general result of these direct measurements of ionic velocity goes to confirm the indirect calculations of the methods of Hittorf and Kohlrausch, in the case, at all events, of simple univalent ions.

Now Kohlrausch finds that the velocity of any one such ion through a dilute aqueous solution is independent of the nature of the other ion present. Thus, for instance, the velocity of chlorine is the same in dilute solutions of

potassium chloride as in solutions of sodium chloride. The velocity under a given electric force is a characteristic property of each ion when moving through a dilute aqueous solution. This result suggests that the ions are independently mobile—that they migrate through the liquid independently of each other.

On this view we must suppose that a large proportion of the whole number of molecules of salt present in a solution is composed of dissociated ions—ions, that is, which are not combined with each other, though they may be linked with solvent molecules. The alternative to this supposition seems to be that the motion of the ions is secured by their passage from molecule to molecule at the instants of inter-molecular collision. On this view, the speed with which the ions worked their way through the solution would depend on the frequency with which collisions occurred. The frequency of collision will depend on the square of the concentration; if the number of molecules be doubled, the number of collisions per second will be four times as great. Hence the velocity of the ions should be greater in concentrated solutions, and the conductivity, which depends on the product of the ionic velocity, and the number of ions, should be proportional to the cube of the concentration. But experiment shows that the velocity of the ions is nearly constant with changing concentration in dilute solutions, and slowly diminishes with increasing strength as the solutions become stronger. We are thus driven back to the idea that the ions migrate independently of each other through the liquid. Much non-electrical evidence pointing to the same conclusion has come to light, and has lent support to the theory of electrolytic dissociation.

I do not propose to enter in this place into a discussion of that theory. But I wish to point out that the evidence, electrical and other, in its favour points merely to a dissociation of the opposite ions from each other; it does not involve the idea of charged particles of, say, potassium or chlorine free from all combination. It may well be that the charged atoms, dissociated from each other, are linked, permanently or temporarily, with one or many molecules of the solvent.

Several facts seem indeed to show that some such combination does occur. If the temperature of a solution be varied it is found that the velocity of the ions alters in about the same ratio as the viscosity of the liquid. Now the viscosity gives the friction which the liquid exerts upon a body moving through it—the dimensions of the body being very large compared with the dimensions of the molecular structure of the liquid. There seems no reason to suppose that the resistance suffered by a single atom, struggling through a crowd of other atoms or molecules, would be related intimately to the ordinary viscosity. In fact, where the structural dimensions of the medium which determine its viscosity are large compared with those of the moving body, it is known that no such relation holds. Thus there is no proportionality between the variation in viscosity of a salt solution when successive quantities of gelatine are added and the variation in the velocity of the ions of the salt. Here the gelatinous structure is probably a sort of fibrous network, very coarse compared with molecular dimensions.

Thus, the approximate proportionality between variation of viscosity with temperature and variation of ionic velocity, indicates that the dimensions of the ions are probably as large as, or larger than, the dimensions of the molecular structure of the solvent. We may perhaps regard the ions as composed of a central charged nucleus, surrounded by a group of solvent molecules. Such a view is supported by Kohlrausch and by Bousfield.

It should be noticed, however, that the solvent molecules cannot remain attached to the charged nucleus throughout its whole journey. The different ionic velocities of potassium, sodium, and lithium, for instance, indicate differences in the amount of the watery ionic envelope. The amount of water transported through a dilute solution of a chloride by these three ions cannot be the

same; it cannot, in each case, be equal to that transported by the chlorine ion. If the water were permanently attached to the nucleus till it reached the electrode, we should get changes in concentration not contemplated by the theory of Hittorf and Kohlrausch, and the migration constants directly determined by Steele and Denison would not agree with those measured by Hittorf. We must suppose, therefore, that the moving ionic system continually sheds some of its watery envelope, and continually replaces it by fresh water molecules.

One of the most interesting properties of these charged ionic systems is their power of causing the coagulation of certain solutions of colloids, such as albumen. If an electrolyte be added to such a solution in sufficient quantity, coagulation at once ensues, and a curious relation between the coagulative power and the chemical valency of the ionic nucleus enables us to obtain some light on the mechanism of the process. Hardy has shown that colloids themselves generally move through a solution when an electric field is applied, the direction of motion depending on the nature and condition of the liquid solvent. It follows that the colloid particles themselves possess an electric charge, and Hardy finds that the effective ion of the coagulating electrolyte is the ion with an electric charge of sign opposite to that on the colloid. It seems that coagulation is effected by the neutralisation of the charge on the colloid. Now a very much smaller quantity of a divalent salt is able to produce coagulation than is necessary in the case of a univalent salt, and the coagulative power of a trivalent salt is greater than that of a divalent salt. As mean values, Linder and Picton give for the coagulative powers of sulphates of univalent, divalent, and trivalent metals the relative numbers 1 : 35 : 1023.

As we saw above, Faraday's experiments show that a univalent ion is associated with one natural unit of electricity, a divalent ion with two such units, and a trivalent ion with three.

Let us suppose that to effect the coagulation of a region of colloid solution, it is necessary for a certain electric charge, equal in amount to that on the colloid particles present and opposite in sign, to be brought within the region. This can only be done by the chance conjunction of ions which, in the absence of an external electric field, must be supposed to be moving in irregular and changeable ways throughout the liquid. If the chance of one ion entering the region be represented by $1/x$, that of two ions entering together will be the product of these separate chances or $1/x^2$, while the chance of the triple event of these conjunctions will be $1/x^3$.

Now, to obtain an equal amount of electricity, we need the presence of 2 trivalent ions, 3 divalent ions, or 6 univalent ions; and, if we work out the problem for solutions containing the same number of molecules, we find that the relative coagulative powers of univalent, divalent, and trivalent solutions should stand to each other in the general approximate ratio of—

$$1 : \beta : \beta^2.$$

The value of the β depends on unknown quantities, such as the effective radius of ionic action, and cannot at present be calculated theoretically. But, by putting β equal to 32, it is easy to see that the law of increase of coagulative power with valency is that we have deduced; for the theoretical numbers—

$$1 : 32 : 1024$$

agree well with Linder and Picton's mean results.

Electric Conductivity of Hydrochloroferic Colloid.—G. Malfitano.—Solutions of hydrochloroferic colloid, when sufficiently dilute, have an electric conductivity whose value is very nearly that of the liquid which remains after filtering through collodion.—*Comptes Rendus*, cxliii., No. 3.

ITALIAN SOCIETY OF SCIENCES KNOWN AS
THE SOCIETY OF THE XL.*

REPORT on the Award of the Matteucci Medal (year 1906),
presented by the Commission composed of the Members
BLASERNA, RIGHI, and ROITI.

JAMES DEWAR, born in 1842 at Kincardine-on-Forth in Scotland, completed his studies and took the first steps in his professorial career in the University of Edinburgh; in 1873 he was appointed Professor of Natural Philosophy at Cambridge, from which post he was promoted Fullerian Professor in the Royal Institution in London, where he is likewise Director of the Laboratory founded in memory of Davy and Faraday.

We shall not pause to enumerate all the contributions which he rendered to the knowledge of aromatic compounds, nor the other important investigations in chemistry by which he initiated his scientific career. But we cannot omit to point out the work which he carried out from 1878 to 1890, for the most part in conjunction with Professor G. D. Liveing, of Cambridge, which work undoubtedly forms part of the finest that has yet been produced in the field of spectrometry. This work is set out in about fifty short notices free from all preconceived ideas and admirable in their experimental genius, enriched with data meriting the highest attention and universally accepted, and fertile in their theoretic bearing and scope. Dewar and Liveing were the first to investigate the phenomena of inversion in many elements; afterwards they studied the influence of temperature on the spectra of the same elements, and the way in which these spectra were modified by the presence of other elements. Extremely interesting are their researches regarding the various spectra of carbon and its compounds, and in relation to the phenomena of synthesis manifested in the electric arc. They, moreover, furnished the first exact determinations of the ultra-violet spectral region, assigning with the utmost care the wave-lengths for a fair number of elements.

Various other problems made evident Dewar's extraordinary experimental ability, and his world-wide fame was secured by the problem, more than any other, of obtaining extremely low temperatures, to which he has indefatigably and courageously devoted himself for more than twenty years, with the satisfaction of seeing his labours crowned by the liquefaction and solidification of hydrogen, which allowed him to study the chemical and physical properties of gases formerly held to be irreducible, when they have changed their state of aggregation.

Having ingeniously contrived means for rendering inconsiderable the losses by evaporation of these new and highly volatile liquids, and thus for preserving them for a length of time in large quantities, he turned this to able account in order to investigate the very varied phenomena which took place at their boiling temperatures, low in themselves, and still further lowered by expansion.

Most extensive is the field covered by Dewar in his studies of this kind; variations of density and cohesion, chemical and photographic actions, phosphorescence and radio-activity, optical properties, thermo-electricity, electric conductivity and inductivity, and magnetic susceptibility. It would take too long to enumerate here the important and partly unexpected results obtained by him, and indeed it is superfluous, as they are present in the minds of all. Let us rather restrict ourselves to accompanying the Matteucci Medal, which we award him, by the wish that, from the 13th which he has already reached, he may descend still further downwards towards absolute zero, and succeed in liquefying even helium.

The Commission:—

P. BLASERNA.
A. RIGHI.
A. ROITI.

Rome, July, 1906.

* Extract from Series 3A, Vol. XIV.

ON THE DISTRIBUTION OF RADIUM IN THE
EARTH'S CRUST.*

By the Hon. R. J. STRUTT, F.R.S., Fellow of Trinity College,
Cambridge.

PART II.—SEDIMENTARY ROCKS.

IN a paper read before the Society on April 5, I gave determinations of the quantity of radium in igneous rocks (see CHEMICAL NEWS, vol. lxxxiii., p. 235). Similar data for sedimentary deposits will now be given to complete my survey of the radium content of the earth's crust.

The limestones examined (oolite, chalk, marble, &c.) were simply dissolved in hydrochloric acid, and the emanation extracted from the solution. All other rocks (including sandstones, clays, slates, gravel) were first fused with sodium carbonate, in exactly the same way as the igneous rocks dealt with in the former paper. I believe that in some cases, clays for instance, this is unnecessary; for determinations made on clay simply treated with hydrochloric acid gave the full quantity of emanation.† But to avoid any doubt, fusion was always resorted to.

The results for sedimentary rocks are given in Table I.

TABLE I.

Rock.	Locality.	Radium per gram., in grms.
Oolite	Bath	5.84×10^{-12}
Oolite	St. Alban's Head . .	4.05 "
Marble	East Lothian	3.87 "
Kimmeridge clay . .	Ely	3.77 "
Oil-bearing sandstone	Galicía	3.04 "
Roofing slate	Wales (?)	2.57 "
Silicified gritty slate	St. Ives, Cornwall . .	2.50 "
Gault clay	Cambridge	2.13 "
Clay	Terling, Essex	1.73 "
Red sandstone	East Lothian	1.68 "
Gravel (fine siftings) .	Terling, Essex	1.42 "
Red chalk	Hunstanton	1.07 "
Flint (large nodules)	Terling, Essex	1.06 "
White marble	Deccan, India	0.54 "
Marble	East Lothian	0.52 "
Chalk	Bottom of pit, Cherry Hinton, Cambs. . . .	0.78 "
Chalk (a)	Top of same pit	0.25 "

(a) This determination was made on 500 grms. of material, in order to get a sufficient leak for measurement.

On comparing these figures with those given in my former paper for igneous rocks (*Proc. Roy. Soc., A*, vol. lxxvii., p. 479, last column but one of the table), it will be observed that the average radium content of sedimentary deposits does not differ appreciably from that of igneous rocks. This is what might be expected on the received view that sedimentary rocks derive their material from the disintegration of igneous ones.

It appears then that the examination of sedimentary rocks for radium gives no reason for altering the estimate of the radium content of the earth's crust formerly arrived at.

I have examined a few other materials which cannot be properly described as rocks, but which are of interest in the present connection.

The results are given below:—

TABLE II.

Material.	Radium per gram., in grms.
Deposit from hot springs, Bath	8.28×10^{-12}
Cambridge tap-water (a)	0.78 "
Sea-salt (approximate determination only)	0.15 "
Boiler crust, Cambridge	0.078 "

(a) This is the quantity of radium which corresponds to the emanation dissolved in 1 c.c. of the water. The radium is not itself present in the water.

* A Paper read before the Royal Society, June 21, 1906.

† The emanation cannot be quantitatively extracted from clay by merely boiling it with water.

It will be noticed that the deposit from the Bath spring is 100 times as rich as any rock. The materials transported by cold water, sea-salt, and boiler crust are, on the other hand, much poorer in radium than any of the rocks.

PART III.—ROCK-FORMING MINERALS.

Igneous rocks are aggregates of many distinct minerals. It was felt that the enquiry as to the distribution of radium in such rocks would be incomplete without some attempt to determine in which of these minerals that element chiefly resides.

Most of the rock-forming minerals can be obtained in large well developed crystals. Such crystals occur for the most part in exceptional localities where crystallisation has been extremely slow, and where the structure of the rocks is on a large scale throughout. In these cases it is easy to obtain any desired quantity of the pure mineral for investigation.

I have examined a number of such specimens of rock-forming minerals for radium. The results are given in Table III. In some cases the quantity of material taken for the experiment proved insufficient to give a satisfactory quantitative measure of the amount of radium in the mineral. This is indicated by a note of interrogation. In other cases no radium at all was detected. In all probability some traces would have been found if more of the mineral had been taken, but the object was to determine whether the mineral made any important contribution to the total radium in the rock. Thus it was not thought worth while to push the examination of accessory minerals, such as ilmenite or rutile, which only occur in small proportions, very far. The quantities of material taken for these experiments are given, so that the quantitative significance of a negative result may be judged.

TABLE III.

Mineral.	Locality where found.	Quantity taken. Grms.	Radium per gram. Grms.
Zircon . . .	Ural Mountains . . .	1	865×10^{-12}
Zircon . . .	North Carolina . . .	1	658 "
Zircon . . .	Brevig . . .	0.690	139 "
Zircon . . .	Kimberley . . .	1.17	74.8 "
Perovskite . .	Magnet Cove, Arkansas	1	197 "
Sphene . . .	? . . .	1	102 "
Apatite . . .	Sweden . . .	8	29.7 "
Apatite . . .	California . . .	4.7	11.0 "
Hornblende . .	? . . .	7.5	4.27 "
Tourmaline . .	Devonshire . . .	11.3	3.32 "
Labradorite . .	Labrador . . .	17	1.1 ?
White felspar .	Nellore, India . . .	20	0.6 ?
White mica . .	Nellore, India . . .	10	1.0 ?
Brown mica . .	Deccan . . .	10	1.0 ?
Brown mica . .	? . . .	10	Nil
White quartz .	Nellore, India . . .	30	Nil
Rutile . . .	? . . .	1	Nil
Ilmenite . . .	? . . .	1	Nil

It will be observed that certain of the accessory minerals, *i.e.*, zircon, sphene, perovskite, and apatite, which occur in granite, are rich in radium. The hornblende, micas, tourmaline, and felspars examined contain much less, while in quartz none could be detected.

Although these experiments throw a certain amount of light on the subject, they are in some respects inconclusive. It is not safe to take these exceptional cases where large crystals occur, as typical; for slow crystallisation is likely to result in more perfect separation of the constituent elements. Moreover, it is difficult to form any idea of the proportion in which the various minerals occur, especially when there has been no opportunity of examining them *in situ*. One cannot tell, for instance, whether enough zircon occurs to account for any large fraction of the radium contained in the whole rock. I have accordingly made some experiments by separating the constituents of an ordinary rock. For this purpose Cornish granite was selected, as being comparatively rich in radium, and

coarse enough to allow of easy separation of the constituent minerals. Sixty-five grms. of Cornish granite was powdered just so far that each particle was seen to be composed of one mineral only, when examined with a magnifier. Bromoform was used to separate the dense minerals from the light ones. The dense minerals, which sank, weighed only 7.5 grms. The rest of the powder, consisting of quartz and felspar, floated on the liquid.

The dense portion consisted mainly of brown mica, but may have contained some zircon enclosed between the flakes, the separation of which by mechanical methods would be impracticable. The dense portion was accordingly digested with hydrochloric acid until the flakes had lost all their colour, nothing but silica remaining. This treatment would leave the zircon behind, as it is not appreciably acted on by hydrochloric acid.

The rock was thus divided into three portions. The quantity of radium in each of these portions was determined by the usual method.

The result was that 1 grm. of Cornish granite contains:—

	Radium (grms.).
In the light portion (quartz and felspar) . .	3.85×10^{-12}
In the heavy portion, soluble in HCl (brown mica)	4.27 "
In the heavy portion, insoluble in HCl (zircon ?)	1.02 "
Total	9.14×10^{-12}

It appears, therefore, that more than half of the radium is contained in the heavy minerals, though these are only one-eighth of the whole mass of the rock. Although the separation by means of bromoform was not perfect, it was, I think, good enough to make it certain that a considerable portion of radium is really contained in the light constituents. As to the heavy minerals, it would not seem that there is enough zircon to account for much of the radium, which chiefly resides in the brown mica.

It appears that radium, or rather its parent, uranium, is not perfectly separated from a rock magma by the crystallisation of the heavy constituents, though considerable concentration in these constituents occurs.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 3, July 16, 1906.

Absorption of Nitrogen by Organic Substances under the Influence of Radio-active Materials.—M. Berthelot.—The author's experiments prove that radio-active materials, to a certain degree, play the same part as an electric current in determining the fixation of nitrogen and oxygen on to organic substances.

Reduction of Molybdenum Dioxide by Boron. Compounds of Boron and Molybdenum.—Binet du Jassonneix.—The reduction of molybdenum oxide by boron, and the union of the two elements, can be obtained under the influence of the electric furnace in crucibles of pure magnesia. Non-carburetted melts are thus obtained, containing proportions of boron up to 46 per cent.. These compounds are attacked by dilute nitric acid.

No. 4, July 23.

Zirconium Silicide, $ZrSi_2$, and Titanium Silicide, $TiSi_2$.—Otto Hönigschmid.—The reduction of zirconium oxide and the double fluorides of potassium and zirconium by the aluminothermic method, and in presence of a large excess of silicon, gives the silicides $TiSi_2$ and $ZrSi_2$.

The latter is in the form of small iron-grey crystals, with a very decided metallic lustre. The mineral acids have no action on this silicide, with the exception of hydrofluoric acid, which dissolves it easily, with evolution of hydrogen. Titanium silicide is also in the form of iron-grey crystals. This substance oxidises only with great difficulty, but it burns in chlorine below red heat. It also is soluble only in hydrofluoric acid.

Alloys of Lead and Calcium.—L. Hackspill.—The author prepares alloys of lead and calcium by the electrolysis of a mixture of chloride and fluoride of calcium, using a cathode of molten lead. The alloys thus prepared are harder and less malleable than lead, and tarnish rapidly in air. When heated in air the calcium oxidises first, giving lime and calcium nitride, which in part protects the lead from oxidation. Water attacks the alloys slowly in the cold, more rapidly when boiling. The author also tries to increase the proportion of calcium in the alloy to 21 per cent by heating it in a vacuum, so as to distil off the excess of lead. At the end of one and a-half hours he obtains an alloy containing 11.8 per cent of calcium; the formula Pb_3Ca_2 requiring the composition $Pb = 88.49$ per cent, $Ca = 11.51$ per cent. The melting-point of this is 775° , and its density 7.6, and the substance is definitely crystalline.

Spectra of Cathodic Phosphorescence of Terbium and Dysprosium Diluted with Lime.—G. Urbain.—Inserted in full.

Radio-active Lead Extracted from Pitchblende.—Jean Danysz.—The author measures the radio-activity of the lead extracted from pitchblende by means of the piezo-electric quartz. To measure the penetrating radiation, he absorbs all the easily absorbable radiation by a sheet of aluminium 0.025 m.m. thick placed some millimetres above the salt. He also verifies the fact that this completely stops the radiation emitted by a sheet of poloniferous silver which is strongly radio-active.

Constitution of Hordenine.—E. Léger.—The production of picric acid during the action of HNO_3 on hordenine shows, not only that this base contains a benzenic radicle, but that its oxyhydrile is directly attached to this radicle. In other words, that this oxyhydril is of a phenolic nature, which can be expressed by saying that hordenine contains the group $C_6H_4<OH$.

A series of experiments, which the author has not yet completed, lead him to suppose that the radicle containing the nitrogen group is due to the intermediary of a chain, $-CH_2-CH_2-$. By this hypothesis the formula of hordenine would be

$C_6H_4<CH_2-CH_2-N<CH_3$, corresponding to the expression $C_{10}H_{15}NO$. The author proposes to verify the exactness of this formula, which he here gives with certain reservations.

Action of Phenyl-magnesium Bromide on the Ethers of the Dialcoylamido-benzoic Acids.—J. Péard.—The author investigates the action of phenyl-magnesium bromide on the ethers of the dialcoyl-amido-benzoic acids. He thus prepares para-dimethylamido- triphenyl- oxy- dihydro- benzofurfurane,

$C_6H_5>C<C_6H_4N(CH_3)_2$, and a certain number of its derivatives, such as the methylic ether, ethylic ether, &c.

Introduction of Dinaphthopyryl and Xanthyl Radicles into Electro-negative Molecules.—R. Fosse and A. Robyn.—The electro-positive radicles, dinaphthopyryl, $CH<C_{10}H_6>O$, and xanthyl, $CH<C_6H_4>O$, can easily be substituted for one atom of hydrogen in various organic electro-negative molecules—such as the β -ketonic ethers, the β -diketones, the malonic and cyanacetic ethers. The positive radicle unites with the nega-

tive radicle—(1) By the simple action of heat on an equimolecular mixture of xanthidrol and β -ketonic or cyanacetic ether; by virtue of its extreme mobility, the hydroxyl of the xanthidrol unites with one atom of hydrogen of the β -ketonic ether to form one molecule of water, whilst the xanthyl unites with the negative radicle. (2) By contact in acetic medium. (3) By double decomposition between the bromide of dinaphthopyryl and the sodium derivative of the β -ketonic ether, the β -diketones, the malonic and cyanacetic ethers.

ERRATA.—Vol. xciii., p. 213, col. 2, line 35 from bottom, for "3 c.c. hydroxylamine hydrochlorate" read "5 c.c." P. 214, col. 1, line 13, for "44.19" read "46.19."

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THE CHEMICAL NEWS.

VOL. XCIV., No. 2440.

REPORT ON OUR PRESENT KNOWLEDGE OF THE CHEMISTRY OF THE GUMS.*

By H. H. ROBINSON, M.A., F.C.S., F.I.C.

The gums are a class of substances characterised by the property of either dissolving in water to form viscid solutions or of absorbing water to form gelatinous pastes; these solutions or pastes on exposure to air lose their water, and dry to hard translucent somewhat glassy masses. The gums are uncrystallisable, and are composed of carbon, hydrogen, and oxygen. As found in nature they contain more or less ash constituents, and sometimes contain a little nitrogen. The nitrogen, if present, is small in amount, and is not regarded as an essential component, and this differentiates them from gelatin, glues, and proteids, which also possess the above properties, but contain a considerable proportion of nitrogen.

The gums occur in plants, and are often found as exudations on the bark or other surfaces; some gums have also been found in animal products. Different views have been held as to the processes by which gum is formed in the plant. One view considers the production of gum part of the normal metabolism of the plant; in the case of tree-gums they are generally regarded as an excretion resulting from the breaking down of cell tissue. In certain cases it has been attributed to the action of a fungus which attacks the tree, and generates an enzyme that penetrates the tissues and transforms the cell-walls, &c., into gum. A third view attributes it to bacterial action, and it is claimed that specific bacteria have been found capable of producing different kinds of gum. The employment of a system of inoculating the trees to cause the production of gum has been suggested, but the evidence in support of it is as yet very slight.

The word "gum" in its earliest use was probably applied to plant exudations which thickened and hardened on the surface of the plant, and thus it has been applied not only to substances which have an affinity for water but also to resins and caoutchouc. As the latter are very different in their composition and properties from the substances of the class described above, it is most convenient not to include them with these.

One of the earliest recorded uses of the word is by Herodotus, who described (about 450 B.C.) how, in Egypt, the embalmers swathed the corpse in strips of linen smeared with gum, which, he adds, the Egyptians generally use instead of glue; he employs the word *κόμμι*, from which the word "gum" is descended. The gums have been familiar substances in European literature from that time to the present, being designated by some form or other of the word *κόμμι*, which itself was not a native Greek word, but was of foreign origin.

The views held regarding the chemistry of the gums since the year 1774, which may be regarded as the period of the dawn of modern science, have passed through three phases.

In the first phase they were regarded as being among the proximate or immediate principles of plants; such a proximate principle being defined as a distinct compound existing ready formed in plants. They were accordingly placed in the lists of such principles, which at that time were not very extensive. It was then imagined that the chemistry of animal and vegetable products was far simpler than we now know it to be. It was known that

the gums were composed of carbon, hydrogen, and oxygen, with possibly some nitrogen.

In the second phase, as analysis appeared to show that the hydrogen and oxygen were in the same proportions as in water, they were considered to be carbohydrates; and when by studying the action of reagents on them it was found that on hydrolysis they yielded various sugars, they were classed as polysaccharides; that is, substances formed of two or more sugar residues united together and differing from the sugars by one or more molecules of water.

In the third phase, by a more careful and systematic series of fractionations and hydrolyses, several of the gum substances have been shown to be built up of the residues of sugar molecules united by an ethereal oxygen attachment to an organic acid, which is different in different gums, and which may be regarded as the nucleus of the particular gum. In other words, they are glycosides of certain organic acids. The number of these sugar residues in a gum compound is considerable, and the natural gum is often a mixture of several gum compounds differing from one another in the number of sugar residues in their molecules. As the attachment is ethereal and not like that of an ester, the gum compounds possess acid properties, since the acid groups are not neutralised by the sugar residues.

This is the most modern view, and doubtless many, if not all, of the gums will be found to be of this nature when fresh examination of them has been made.

It must be understood, however, that these phases are not sharply marked off from one another in sequence of time, the germs of the later idea being often found in the records of earlier investigations.

In the early part of the Nineteenth Century a good many gums were known, the most familiar of which were gum-arabic, gum tragacanth, gum Bassora, gums from the genus *Prunus*, such as cherry-tree gum, and the mucilages or gum solutions obtained from linseed and from quince seed.

At that period the activity awakened by the new ideas in chemistry was the cause of various attempts to ascertain the nature of the substances that form the different gums. The work then done resulted in the descriptions of the properties of a few gum substances believed to be individual chemical compounds, to which the names *bassorin*, *cerasin*, and *arabin* were given. After these names had been assigned chemists, dominated by the idea that the number of organic compounds was only small, on investigating a gum identified its constituents with one or more of these substances. As these identifications rest on only a few simple properties but little weight attaches to them. In fact, it now appears that the number of gum compounds is very considerable; consequently in reading the literature of the last century statements that the author had found the presence of arabin, or cerasin, or bassorin, &c., do not throw any certain light on the nature of the substance found, as it cannot be safely inferred that it is the same substance as the arabin, or cerasin, or bassorin, &c., found in another natural product by another author.

It may be of some interest to trace the origin of these names so often attached in the last century to the components of the different gums.

Bassorin.—In 1811, Vauquelin published an examination of gum Bassora, and in the same year Pelletier, who was engaged in examining several gum resins, published a paper in which he proposed the name *bassorine* for the substance constituting the gum Bassora described by Vauquelin, since he believed he had found the same substance in the gum resins. Gum Bassora appears to be a gum having properties somewhat similar to those of tragacanth, but not to be so highly valued. It derives its name from the Turkish port now called Basra, at the head of the Persian Gulf, from which there is a considerable export of gums. A gum Bassora is still quoted in the London market reports, but whether it is the same gum as that examined by Vauquelin, or whether it really comes

* A Paper read before the British Association (Section L), York Meeting, 1906.

from Basra, is not easy to say, since trade terms of the kind are often misleading.

Cerasin.—In 1812, John, who was aware of Vauquelin's work, published an examination of several gums derived from the genus *Prunus*, and gave the name of *cerasin* or *prunin* to the gum substance he obtained from the fruit of the plum known as Mirabel, and also from the stem of the wild cherry-tree, *Prunus avium*. He found that the gum of the sweet cherry-tree was of a different nature. The term "prunin" did not come into use, but "cerasin" has often been used.

Arabin and Para Arabin.—In 1833, Chevreul, in reporting on a memoir on the gums written by Guérin, gave the name *arabine* to the gum substance of gum-arabic and of gum Senegal, and remarked that if *cerasin* should prove to be identical in composition with arabin it ought to be called *para arabine*.

Roughly speaking, it may be said that in the descriptions of the gums the part soluble in cold water was put down as arabin and the part insoluble in cold water was put down as *cerasin* or *bassorin*.

Metagummic Acid and Gummic Acid.—In 1860, Frémy published a paper in which he described a substance obtained by pouring a strong solution of gum-arabic on to concentrated sulphuric acid. This substance is insoluble even in boiling water, but alkalis cause it to dissolve, and then acids do not re-precipitate it from the solution. He gave the name *metagummic acid* to the insoluble acid and *gummic acid* to the soluble acid produced by the action of alkalis on metagummic acid and also existing in soluble gum. He remarks that these experiments modified all the ideas then held concerning gum-arabic, which up to then had been considered as a neutral substance comparable to dextrin, but that it now appeared that the natural gum was a lime salt of an acid. It was, in fact, gummate of lime, and the insoluble natural gum *ceresine* was metagummate of lime. It should be mentioned that the term "gummic acid" has also been used for quite a different substance prepared by Reichardt.

Arabic Acid.—That gum-arabic was largely composed of an acid had already been discovered by Neubauer and announced in 1854 and 1857, although Frémy was not aware of this. Neubauer made analyses of the acid obtained by freeing gum-arabic of its ash constituents, and also of the salts of this acid, to which he gave the name *Arabisäure*.

Metarabic Acid.—Frémy's term metagummic acid seems to have been changed into *metarabic acid* by later writers, no doubt because his gummic acid was the same as the arabic acid previously described by Neubauer.

As early as 1810, Gay-Lussac and Thénard had analysed gum and had put it in the same class as sugar and starch, stating that these substances were composed of carbon united to hydrogen and oxygen, which were in the same proportions as in water; that is to say, they put it in the class of compounds now called carbohydrates.

An important step in the elucidation of the problem of the constitution of gums was Scheibler's discovery, published in 1868 and in 1873, of a new sugar, *arabinose*, obtainable both from gum-arabic and from a gummy substance yielded by sugar-beet. He also noticed the concurrent liberation of an acid with the sugar, but does not seem to have investigated it further. As early as 1832, however, Guérin had obtained a sugar from gum-arabic by the action of sulphuric acid.

Arabinon, galactose, xylose, fucose, and tragacanthose are other sugars which have been obtained from gums by hydrolysis.

Up till comparatively recently, the gums have been placed among the carbohydrates together with cellulose, starch, and dextrin, and have had the formulæ $(C_6H_{10}O_5)_n$ and $C_{12}H_{22}O_{11}$ assigned to them, and, in fact, this view has not yet been abandoned by the text-books. O'Sullivan, however, has shown that this view of their nature is mistaken, and that the gums are really acids of high molecular weight, and are constituted of an acid grouping forming a

nucleus to which are attached a number of the residues of various hexoses, pentoses, and bioses; these residues being linked on to the acid nucleus by an ethereal oxygen attachment, just as the dextrose and levulose are joined in cane-sugar. In some cases the linking is by two oxygen atoms, and reaction with two molecules of water occurs when the sugar residue is broken off by hydrolysis.

He first dealt with gum-arabic, and in 1884 showed that it contained an acid nucleus of the formula $C_{23}H_{38}O_{22}$, to which in a later paper he gives the name *arabic acid*; it is the λ -*arabinosic acid* of the 1884 paper. The gum substance itself is an acid composed of this nucleus joined to the residues of a number of galactose and arabinose or arabinon molecules; arabinon, $C_{10}H_{18}O_9$, being a biose or disaccharide formed by the union of the residues of two arabinose molecules. On submitting the gum to hydrolytic action of varying degrees of intensity more and more of the sugar residues are split off, and acids of lower and lower molecular weight and of higher and higher neutralising power are obtained until arabic acid is reached. This acid is of considerable stability, and requires strong hydrolytic action to break it up, and it then appears to suffer a great degree of disintegration. In the light of the pentose nature of arabinose announced in 1887 by Kiliani, O'Sullivan assigns to the gum substance the formula $2C_{10}H_{16}O_{8.4}C_{12}H_{20}O_{10}C_{23}H_{38}O_{18}$, and names it *di-arabinan-tetragalactan-arabic acid*. In this "arabinan" and "galactan" stand for two molecules of arabinose and galactose respectively minus two molecules of water, the termination "-an" indicating the anhydride of the corresponding sugar. The arabic acid nucleus appears in this formula with four molecules of water less than in the free acid, indicating the occurrence of four double oxygen attachments between the sugar residues and the nucleus acid, and showing that sixteen molecules of water are required for complete hydrolysis to arabinose, galactose, and free arabic acid. In the natural gum of course the acid is more or less neutralised by the potash, lime, and magnesia of the ash constituents of the plant. The "arabic acid" of O'Sullivan thus denotes the nucleus acid and not the acid of the natural gum substance; since the latter acid differs in different specimens of gum, this seems to be an advantageous change, especially as it permits of descriptive names being given to the varying natural gum acids.

A gum known in commerce as Geddah gum was next examined by O'Sullivan; it resembles gum-arabic in being soluble in water, but it is dextrorotatory, whilst gum-arabic is levorotatory. He found that it is a mixture of several gum acids which are constituted of the radicles of galactose and of arabinose or arabinon attached in considerable numbers to a nucleus acid, to which the name *geddic acid* is given. Geddac acid is an isomer of arabic acid, $C_{23}H_{38}O_{22}$. The acids forming the mixture of which the gum itself is composed are of high molecular weight, and differ from one another in the number of arabinon molecules they contain, and consequently in their rotatory power.

The third gum investigated was tragacanth; this, like Geddah gum, was found to be a mixture of several gum acids. It can be separated into a group of acids which remain in solution in dilute alcohol and an insoluble portion for which the old name *bassorin* is appropriated. The acids of the soluble group were found to be built up on a nucleus acid very similar, if not identical with, geddic acid by its union with galactose and arabinose residues. The constitution of the insoluble portion *bassorin* has not yet been completely worked out, but it yields a nucleus acid of the formula $C_{14}H_{20}O_{13}$, to which the name *bassoric acid* is given, and intermediate acids formed of this acid united to the residues of xylose and of a new pentose sugar named *tragacanthose*.

It has been observed that in the case of the gum from sugar-beet the gum obtained in one season frequently differs in rotatory power from that obtained in another season, and that in the case of gum-arabic different samples

also differ in this respect. The explanation of this was discovered in the work on Geddah gum; the cause lies in the fact that in these varying gums the number of sugar residues attached to the nucleus acid varies, or in some cases it may be that the gums contain mixtures of the same gum acids, but in different proportions.

It was found that in a series of gum acids containing arabinans and galactans in varying numbers brought to geddic acid that there were indications that the rotatory power varied fairly regularly in a series, thus:—

Series I.

Mon-arabinan-tri-galactan-geddic acid ..	[α] _D +37°
Di- " " " " ..	+43°
Tri- " " " " ..	+49°
Tetr- " " " " ..	+59°

Series II.

Tri-arabinan-tetragalactan-geddic acid ..	+80°
Pent- " " " " ..	+90°
Hept- " " " " ..	+100°
Non- " " " " ..	+110°

Series III.

Tri-galactan-geddic acid	+20°
Tetra- " " " " " " " " " " ..	+22°
Penta- " " " " " " " " " " ..	+30°

The principal constants in identifying a gum acid are its ultimate composition, its neutralising power for bases, and its rotatory power for polarised light. As such acids do not crystallise fractional precipitation must be resorted to in order to prove their individuality. Determinations of the amount of mucic acid they yield and also of the amount of furfural are helpful. In separating the nucleus acid and in preparing intermediate acids lying between the natural gum acid and the nucleus, hydrolyses of varying intensity must be used followed by precipitation with alcohol and purification by means of dialysis. Sometimes it is more convenient to precipitate as barium salts instead of as the free acids.

There is no doubt that in future work on the gums the methods adopted by O'Sullivan should be followed, and that a determination, not only of the sugars they yield should be made, but also of the nature of the nucleus acid. In fact, a great deal of investigation is required to bring our knowledge of other gums up to the level of O'Sullivan's discoveries in the case of gum-arabic, Geddah gum, and tragacanth.

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THE

STUDY OF HYDRO-AROMATIC SUBSTANCES.*

(Concluded from p. 91).

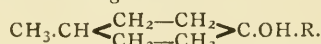
RECENT WORK ON HYDRO-AROMATIC SUBSTANCES.

By Professor A. W. CROSSLEY.

Hydrocarbons.—In a paper entitled "Derivatives of Cyclohexene (*Ann. Chim. Phys.*, 1905, [8], vi., 200) Brunel gives a *résumé* of work already published, together with a description of certain new derivatives.

1 : 2-, 1 : 3-, and 1 : 4-dimethyltetrahydrobenzenes have been obtained by the action of zinc chloride on the hydroxydimethylhexahydrobenzenes mentioned below (Sabatier and Mailhe, *Comptes Rendus*, 1905, cxli., 20). They give the corresponding hexahydrobenzenes when treated with hydrogen in presence of reduced nickel.

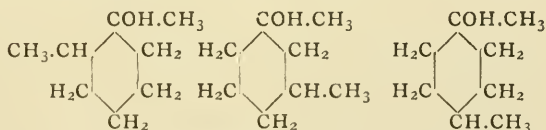
Alcohols.—4-Keto-1-methylhexahydrobenzene reacts energetically with organo-magnesium compounds (Sabatier and Mailhe, *Comptes Rendus*, 1906, cxlii., 438) to form tertiary alcohols of the general formula—



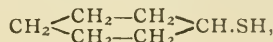
Alcohols in which R = CH₃, C₂H₅, C₃H₇, C₅H₁₁, C₈H₁₇, C₆H₅, and C₆H₅.CH₂ are described, and also the substituted tetrahydrobenzenes obtained from them, generally by the dehydrating influence of zinc chloride. An exception was noted in the case of magnesium isobutyl bromide, which gives rise almost exclusively to butylene and hydroxymethylhexahydrobenzene.

4-Hydroxy-1 : 2-dimethylhexahydrobenzene, 4-hydroxy-1 : 3-dimethylhexahydrobenzene, and 2-hydroxy-1 : 4-dimethylhexahydrobenzene have been synthesised by passing the corresponding xylenol with excess of hydrogen over reduced nickel heated to 190–200° (Sabatier and Mailhe, *Comptes Rendus*, 1906, cxlii., 553). In the cases of the xylenols with the methyl groups in the 1 : 2- and 1 : 3-positions, large amounts of the corresponding xylenes are formed, whereas with the 1 : 4-compound the formation of xylene was not observed, and the hydration mixture consisted of 90 per cent of the desired alcohol and 10 per cent of the corresponding ketone.

In the last Report (1905, p. 155) the hydrogenation of the three cresols was referred to (*Comptes Rendus*, 1905, cxl., 350). Sabatier and Mailhe have now shown that by treating the ketones obtained in this manner with magnesium methyl iodide, good yields of the three following hydroxydimethylhexahydrobenzenes are obtained (*Comptes Rendus*, 1905, cxli., 20):—



Cyclohexylmercaptan has been described by Borsche and Lange (*Ber.*, 1906, xxxix., 392) as a highly refractive liquid of mercaptan-like odour, formed when the sulphon



chloride, obtained by the action of phosphorus pentachloride on potassium hexahydrobenzenesulphonic acid, is reduced with zinc and hydrochloric acid.

Cyclohexylxanthate, C₆H₁₁.S.CS.OC₂H₅ (*Ber.*, 1906, xxxix., 392), is formed by the interaction of potassium xanthate and cyclohexylbromide, and is converted by ammonia into cyclohexylmercaptan and xanthamide.

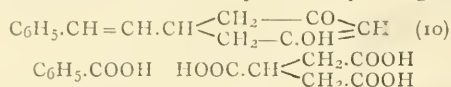
Amines.—Sabatier and Senderens (*Comptes Rendus*, 1905, cxl., 482) have shown that by the hydrogenation of

* Report of the Committee, consisting of Dr. E. Divers (Chairman), Professor A. W. Crossley (Secretary), Professor W. H. Perkin, Dr. M. O. Forster, and Dr. H. R. Le Sueur. Read before the British Association (Section B), York Meeting, 1906.

benzonitrile in presence of nickel at 200°, ammonia and toluene are almost exclusively formed. Frebault (*Comptes Rendus*, 1905, cxl., 1036) now proves that, under modified conditions, the reduction takes place similarly to that of the aliphatic nitriles, and that primary and secondary aromatic amines can be thus obtained. Benzonitrile gives rise to benzylamine and dibenzylamine in approximately equal amounts, and *p*-tolunitrile to *p*-methylbenzylamine and di-*p*-methylbenzylamine.

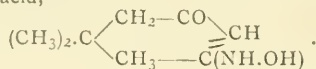
Ketones.—As a further instance of the use of Grignard's reaction, the preparation of cyclohexylacetone may be quoted. Though this substance is not obtainable by the interaction of chlorohexahydrobenzene and ethylsodioacetate, it may be produced by the action of hexahydrobenzylmagnesium iodide on acetaldehyde (Freundler, *Comptes Rendus*, 1906, cxlii., 343).

Dihydroresorcin.—Ethyl malonate combines with cinnamylideneacetone (Vorländer and Gröbel, *Annalen*, 1906, cccxlv., 206) to give cinnamylidenedihydroresorcin (10), which on oxidation with potassium permanganate is

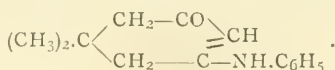


converted into benzoic and tricarballic acids; hence the addition of the elements of ethyl malonate must have taken place at the $\alpha\beta$ -position relative to the carbonyl group. As this addition may be influenced by the tendency to form a six-ring cinnamylacrylic acid, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}:\text{CH}:\text{CH}\cdot\text{COOC}_2\text{H}_5$, where no ring formation is possible, was substituted for cinnamylideneacetone, but again addition took place at the $\alpha\beta$ -position.

Dimethyldihydroresorcin (and also probably phenyldihydroresorcin) gives rise to a crystalline and an amorphous oxime (Gittel, *Cent. Blatt.*, 1896, [1], 33). The former can be converted into a dioxime, whereas the latter cannot, nor does it give an acetyl derivative, which makes it appear probable that it has the constitution of a hydroxamic acid,—

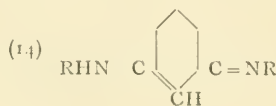
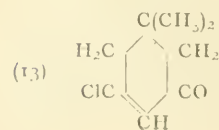
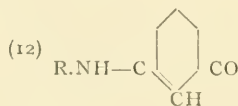
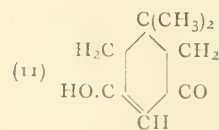


On the other hand, both oximes have faintly acid properties, and may therefore be stereoisomerides. Dimethyldihydroresorcin gives a monophenylhydrazone and also a mono-anilide, which behaves in a similar manner to the



amorphous oxime, in not condensing with a second molecule of aniline to form a di-anilide, nor does it yield an oxime, but it gives an acetyl derivative. The compounds formed by the condensation of dimethyldihydroresorcin with *o*- and *p*-toluidine and α -naphthylamine are also described.

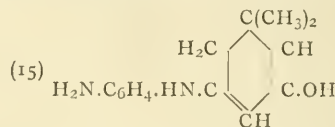
Work of a similar nature, but more comprehensive, has been carried out by Haas (*Journ. Chem. Soc.*, 1906, lxxxix., 187), who shows that dimethyldihydroresorcin (11) condenses with only one molecule of a primary base (ammonia, aniline, or *p*-toluidine), water being eliminated



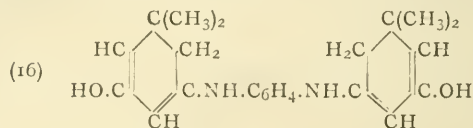
between the hydroxyl group of the dihydroresorcin and a hydrogen atom of the amino-group, to give a compound of the type of Formula 12. On the other hand, chloroketodimethyltetrahydrobenzene (13) reacts directly with two molecules of a primary base, yielding a compound of the type of Formula 14.

Neither dimethyldihydroresorcin nor chloroketodimethyltetrahydrobenzene reacts with secondary amines. The replacement of the hydroxyl group in dimethyldihydroresorcin by a basic group, such as NH_2 , $\text{C}_6\text{H}_5\cdot\text{NH}$, or $\text{C}_7\text{H}_7\cdot\text{NH}$, causes the remaining ketonic oxygen atom of the dihydroresorcin to become hydroxylic, as shown by the colour reactions of the resulting substances with ferric chloride and their behaviour towards phosphorus trichloride. If, however, the substituting group is rendered more acidic by the introduction of an acetyl group, this second oxygen atom becomes ketonic and is able to condense with semicarbazide. The mono-derivatives produced from dimethyldihydroresorcin can be converted into the derivatives directly obtainable from chloroketodimethyltetrahydrobenzene either by condensation with a second molecule of the primary base in presence of zinc chloride, or by the action of the phosphorus haloids.

In a second communication (*Journ. Chem. Soc.*, 1906, lxxxix., 388), it is shown that molecular proportions of dimethyldihydroresorcin and a primary diamine (*m*- or *p*-phenylenediamine) interact to give an 80 per cent yield of the simple condensation product (15), but, in addition,

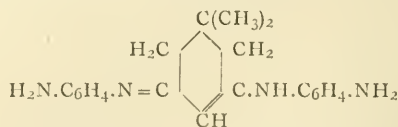


there is also formed a small amount of the compound (16)



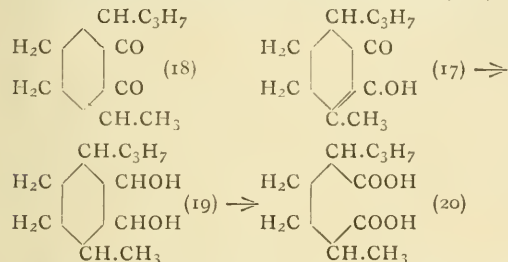
resulting from the condensation of two molecules of the dihydroresorcin with one of the diamine. The compounds of Formula 15 function as di-acid bases, giving rise to dihydrochlorides, which react with one molecular proportion of platonic chloride to form platinum salts; they are insoluble in water, but dissolve in alcohol to form neutral solutions which produce with ferric chloride a reddish brown coloration; with acetic anhydride they yield mono-acetyl derivatives only, which still give a colour reaction with ferric chloride. The di-substituted phenylenediamines (16) are also di-acid bases having a neutral reaction; they are not acetylated by boiling with acetic anhydride, and may be re-crystallised without change from glacial acetic acid; in alcoholic solution they give with ferric chloride a reddish yellow colour.

Chloroketodimethyltetrahydrobenzene condenses at once with two molecules of *m*-phenylene diamine to give the hydrochloride of a base having formula—



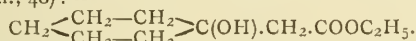
During the investigation of the above-mentioned substances it has been shown that the numbers obtained for the percentage of nitrogen were from 2 per cent to 5 per cent too high for the calculated values (*Journ. Chem. Soc.*, 1906, lxxxix., 570). This discrepancy has been proved to be due to the presence of marsh gas, and a method for obviating the difficulty has been devised.

A further investigation of buccocamphor (diosphenol) has shown it to possess a constitution closely resembling the dihydroresorcins (Semmler and MacKenzie, *Ber.*, 1906, xxxix., 1158). It has the molecular formula $C_{10}H_{16}O_2$, and is a ketone alcohol (17) or diketone (18) containing a hexamethylene ring, with methyl and isopropyl groups in the 1:4-position, and in which the double bond must be attached to the carbon atom carrying the methyl group.



On heating with hydrogen chloride, buccocamphor is quantitatively converted into thymol, and on reduction with sodium in alcoholic solution it yields a glycol (19), which on oxidation, is converted into α -methyl- α' -isopropyl-adipic acid (20), thus definitely establishing its constitution. The authors have succeeded in synthesising buccocamphor by treating hydroxymethylenementhone with ozone.

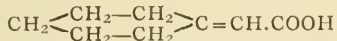
Acids.—Ketohexahydrobenzene condenses with ethyl bromoacetate under the influence of magnesium to give ethyl cyclohexanolacetate (Wallach, *Annalen*, 1905, cccxlili., 40):—



By loss of water and subsequent hydrolysis, cyclohexene-acetic acid is obtained, which, when oxidised with potas-

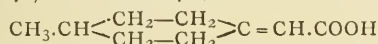


or—

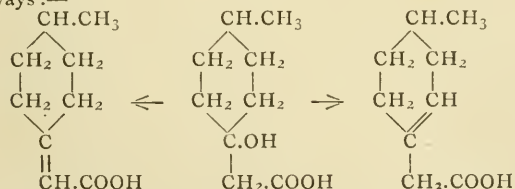


sium permanganate, gives a non-aldehydic compound containing seven carbon atoms.

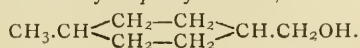
Marckwald and Meth have described an acid believed by them to be 1-methylcyclohexylideneacetic acid (*Ber.*, 1906, xxxix., 1171). It melts at 41° , and has been resolved into



active modifications by fractional crystallisation of the cinchonine salts. It was obtained by the removal of the elements of water from methylcyclohexanolacetic acid, which, as pointed out by Perkin and Pope (*Proc. Chem. Soc.*, 1906, xxii., 107), may take place in one of two ways:—



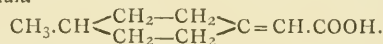
These latter authors have been engaged in an attempt to prepare a substance which, while not containing an asymmetric carbon atom, is yet capable of existing in optically active modifications, and one of the substances selected for examination was methylcyclohexylideneacetic acid. This was prepared from ethyl hexahydro-*p*-toluate as starting point, and which on reduction with sodium and alcohol gives hexahydro-*p*-tolylcarbinol,—



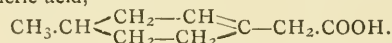
This carbinol is readily converted into hexahydro-*p*-tolyl bromide, which, when heated with potassium cyanide and the product hydrolysed, yields hexahydro-*p*-tolylacetic acid,—



Bromine acts on the corresponding acid chloride with formation of α -bromohexahydro-*p*-tolylacetic acid, and the ester of this bromo-acid is decomposed by boiling with diethylaniline into hydrogen bromide and ethyl methylcyclohexylideneacetate. On hydrolysis, the free acid is obtained, melting at $70-71^\circ$, and the method of preparation leaves no doubt that its constitution is represented by the formula—

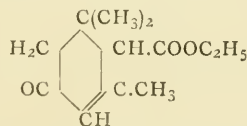


The acid described by Marckwald and Meth is possibly the isomeric acid,—



Chloro- or iodo-hexahydrobenzene reacts with ethyl sodiocyanacetate or ethyl sodiomalonate in xylene solution, and from either of the resulting condensation products cyclohexylacetic acid may be obtained on hydrolysis (Freundler and Damond, *Comptes Rendus*, 1905, cxli., 593).

Ethyl isophoroncarboxylate (D.R.P. 148080), obtained by the condensation of ethyl isopropylideneacetate and ethyl sodioacetate, is a δ -ketonic ester with the following constitution (Merling, *Ber.*, 1905, xxxviii., 979):—



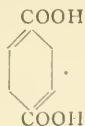
By reduction with sodium and alcohol, a mixture of stereoisomeric hydroxy acids is produced, which does not consist of one *cis*- and one *trans*-acid, as stated in the patent, but of three pairs of *cis-trans*-isomeric acids, in all therefore of six acids, all of which have been isolated. By heating alone or with dehydrating agents three different stable crystalline lactones were obtained, showing that in the parent ketonic acid the carboxyl and carbonyl groups occupy a *para*-position relatively to one another. A further proof of this is afforded by the fact that the lactones are oxidised by Beckmann's solution to three stereoisomeric dihydroisophoroncarboxylic acids, which distil without decomposition *in vacuo*, and do not lose carbon dioxide on heating to 200° in air.

Abati and Bernardinis have isolated two new hydrophthalic anhydrides by the reduction of sodium phthalate with sodium amalgam (*Journ. Chem. Soc.*, Abst., 1905, [1], 599). *Cis*- Δ^3 -tetrahydrophthalic anhydride crystallises in white scales, and on heating to 220° to 230° is transformed into Δ^4 -tetrahydrophthalic anhydride.

Δ^1 :3-Dihydrophthalic anhydride melts at 58° , and on heating to 225° is transformed into another anhydride, which could not be identified.

The *trans*-hexahydroisophthalic acid, previously described (*Journ. Chem. Soc.*, 1891, lix., 808) as melting at 120° to 122° , has been proved by Perkin and Goodwin (*Ibid.*, 1905, lxxvii., 841) to be a mixture of the *cis*- and *trans*-acids, which can be separated by dissolving in a considerable excess of ammonia, and heating for some hours with calcium chloride, when a quantity of the calcium salt of the *cis*-acid is obtained. After repeating this process several times, the mother-liquor yielded pure *trans*-hexahydroisophthalic acid melting at 148° . When the pure *trans*-acid is treated with phosphorus pentachloride and then bromine, 1:3-dibromo-*trans*-hexahydroisophthalic acid is produced, which, on treatment with methyl alcoholic potash, gives a dihydroisq-

phthalic acid, whose constitution is probably represented by the formula—



It is isomeric with the acid previously obtained from 3:4-dibromohexahydroisophthalic acid by similar treatment.

Chlorohexahydrobenzene readily forms a Grignard compound with magnesium (Borsche and Lange, *Ber.*, 1905, xxxviii., 2766), which, when acted on with dry sulphur dioxide, yields magnesium hexahydrobenzenesulphinate. This latter substance, on oxidation with potassium permanganate, gives a mixture of dicyclohexanesulphone and the potassium salt of hexahydrobenzenesulphonic acid. The free acid crystallises from alcohol, melts at 90° to 92°, and gives a corresponding acid chloride, anilide, and ethyl ester.

THE LATEX OF *DYERA COSTULATA*.*

By Prof. W. A. TILDEN.

EARLY in May last I received from a correspondent in Singapore a sample of the latex of *Dyera Costulata* to which a small quantity of ammonia had been added to keep it from coagulating. It remains a white creamy fluid of specific gravity 1.11, miscible with water. I am without information as to the reaction of the original fluid with test-papers. It is rare to find vegetable juices exhibiting an alkaline reaction, but I am disposed to believe that this latex in the fresh state possesses slight alkalinity, as it is coagulated sooner or later by all acids without agitation. But, as in milk, the suspended particles unite when the liquid is violently shaken. It is also coagulated by admixture with strong solution of common salt, and when warmed with an equal volume of 20 per cent solution of soda.

Heated to a temperature of 70° to 80° C. solidification does not occur except at the surface, where a skin forms, and even on boiling no immediate change takes place.

The milk as received yielded about 44 per cent of solid by coagulation with hydrochloric acid.

The aqueous liquid filtered from the coagulum contains a small quantity of a substance which reduces Fehling's solution only after it has been heated for a few minutes with hydrochloric acid. Whether this is cane-sugar or a glucoside I have not yet ascertained. The amount of proteid present is very small.

The coagulated solid is tough, but contains only a very small quantity of rubber substance, as it is almost entirely soluble in alcohol or acetone.

Dyera Costulata is reputed to be the botanical source of the white gutta now quite familiar under the name of "Pontianak," the port in Borneo from which it is exported to Europe. Pontianak contains a small quantity of rubber mixed with two or more substances, of which at least one, melting-point 173°, is crystallisable from alcohol. This analysed in my laboratory gave as the mean of several combustions C = 81.2 and H = 11.0 per cent. This corresponds roughly to a formula $C_{14}H_{22}O$, which requires C = 81.5, H = 10.7. The molecular weight, 206, required for this is, however, much less than the result of observations on the freezing-point of the benzene solution. These gave as a mean 322.

The crystalline substances contained in gutta have been supposed to be related to lupeol, but this can hardly be said to be definitely established.

Likiernik (*Ber.*, xxiv., 185) found in lupeol 84.01 C,

11.38 H, and melting-point 204°. As to the process by which caoutchouc and the associated substances are formed in the latex, nothing seems to be known, but I incline to the view that they are probably formed in the laticiferous vessels by the rupture of molecules of compounds of the nature of tertiary alcohols with the production of water and the hydrocarbon or other substance. The readiness with which terpin splits into terpineol and water by the action of minute quantities of acid is an analogous process.

Note added August, 1906.—My attention has since been drawn by Professor P. van Romburgh to a paper of his in the *Proceedings of the Royal Academy of Sciences of Amsterdam* for June, 1905, in which lupeol acetate and cinnamate are recognised as constituents of gutta-percha and pontianak.

UTILISATION OF NITROGEN IN AIR BY PLANTS.*

By T. JAMIESON, F.I.C., Aberdeen.

THE question whether plants can absorb and assimilate the free nitrogen of air is perhaps the most important question of science bearing on agriculture. It has occupied the attention of eminent chemists from early times, in particular Priestley, De Saussure, Boussingault, Ville, Liebig, and finally, Lawes, Gilbert, and Pugh conjointly at Rothamsted. The question has been answered in the negative, and in the positive almost alternately, but on the negative results of experiments by Boussingault and Lawes the doctrine generally prevails—that plants can not absorb and utilise free nitrogen.

Doubts, however, have frequently arisen in regard to the soundness of this doctrine, in consequence of what appeared to be contradictions given by the general practice of agriculture, as well as by systematic trials, and also by a consideration of Nature's methods and of natural or wild growth. In particular, it was contradicted by the circumstance frequently found, that if legume crops were alternated with cereal crops, good crops were obtained for many years in succession without the application of any nitrogenous manure, and without lowering, but rather increasing, the nitrogen in the soil, and that although large quantities of nitrogenous matter were carried off the land yearly in the form of crops.

In 1885, Atwater, in America, found by careful trials that legumes did acquire nitrogen from air, but he could give no explanation of the nature, or of the seat of the process; consequently, perhaps, his results have been almost ignored, the opposite idea having gained so firm a hold.

In 1887, Hellriegel and Wilfarth in Germany confirmed this power of legumes, but they added the explanation that it was due to the agency of the numerous nodules that are usually found on the roots of legumes. They affirmed that these nodules contain bacteria which, they assumed, absorb the nitrogen of the air in the soil, and change it into a form on which the legumes can thrive, the bacteria themselves being at the same time nourished by the legume, thus indicating a mutual aid or symbiotic existence. It has since, however, been shown by several observers that what were regarded as bacteria are only disaggregated particles of abnormal tissue, and this being the case, bacterial action does not explain the method of absorption of nitrogen. Further, and in particular, it has been found by Franck, in Germany, that if legumes are grown in sterilised soil, no nodules are formed; and yet there is the same evidence of absorption of nitrogen. It thus appears that the absorption must be performed by the

* A Paper read before the British Association (Section B), York Meeting, 1906.

* Abstract of a Paper read before the British Association (Section B), York Meeting, 1906.

plant itself. Therefore, if the legume plant can of itself absorb nitrogen, it appeared probable that all plants can do so to a lesser or a greater extent, but no satisfactory evidence to this effect existed, although Franck found a small grain on colza and oats.

Franck also found that the amount of nitrogen absorbed varied in accordance with the vigour of the plant, and pointed out that the conclusions of Boussingault and Lawes were vitiated by being based on "atrophied" plants. Their experimental plants were grown under abnormal conditions, *i.e.*, in water or sterilised soil and confined air, and in each case they were so very small that they must have been feeble or sickly, and therefore not fitted to display the abilities of vigorous plants grown under natural conditions.

Atwater's trials, on the other hand, were made under more natural conditions, *i.e.*, in sterilised sand, the plants being exposed to air; acting thus, vigorous plants were produced and he found a material gain of nitrogen. His trials also confirmed Franck's conclusion, that the more vigorous the plant the larger the gain in nitrogen.

In view of Hellriegel's investigations, which opposed the conclusions of Lawes and Boussingault, Lawes made further trials and admitted the gain in nitrogen by legumes, adopting, however, the nodule or bacterial explanation of it. But Franck's trials, and Atwater's trials on plants without nodules, obviously nullifies that explanation, and necessitates the conclusion that the plants themselves in one way or other absorb nitrogen. This being the case, Lawes' conclusion, and consequently also Boussingault's conclusion, is undermined by these and by Lawes' own subsequent trials, and the prevailing doctrine that plants cannot absorb and utilise nitrogen from air is thus deprived of support.

Both Atwater and Franck, however, failed to find the part of the plant or the method by which the nitrogen was absorbed; but Franck, who had thoroughly investigated and considered the subject in all its bearings, concluded by anticipating that an organ would be found on plants fitted to absorb nitrogen.

It is the finding of this organ that is the special subject of the paper now submitted. That the organ has not been previously found is probably due to the very great difficulty in detecting it on the mature cultivated plants, and more especially on the legumes, to which, as the most nitrogenous of cultivated plants, attention would in all probability have been the first and specially directed. It so happened that several years ago I had analysed a large number of wild plants, and found that some of them contained a much larger proportion of nitrogen even than legumes; if therefore a nitrogen absorbing organ existed it would probably be conspicuous on such plants, and by far the most likely part of the plant to bear them would be the leaves. These anticipations turned out to be correct. On examining the plant highest in nitrogen, namely, *Spergula arvensis* (or common spurrey), organs were observed whose peculiar structure appeared admirably adapted for nitrogen absorption in the form of short, blunt, horizontally sectioned hairs hoisted up into the air, the highest section of which was found to contain, in the early stage, greenish chlorophyll-like matter, which was separated from the air only by a most delicate film. The application of the usual tests for albumen showed very conclusively that these green tips or highest sections were manufactories of albumen, for while the youngest ones failed to respond to the tests, more advanced hairs responded distinctly; different stages were found corresponding to the age of the hair, some responding to the tests very conspicuously, others were found to be gorged with albumen, and still older hairs were seen to be discharging the semi-solid albuminous matter down through the lower sections. A circular space surrounds the sections, and into this space is continuously discharged liquid albuminous matter, which passes into the internal channels of the leaf, the sections forming the purpose of an ingenious filter.

It remained to ascertain whether similar organs exist on

the other wild plants high in nitrogen, *viz.*, chickweed and nettle, and examination clearly proved their existence in abundance. They showed the same essential characters as above described, but varied more or less in form. Familiarity with the character of the organ being thus acquired, cultivated plants were examined, choosing in the first place the bean, but no sign of the organ could at first be detected on the matured leaves. Ultimately one was found nearly embedded in the tissue; the difficulty in finding it explained the failure of other investigators to discover the method or organ of absorption. When, however, a seedling plant was grown, the youngest leaves showed on examination essentially the same organs, not occasionally, but in profusion. It is on the youngest leaves of plants that the organs have to be sought, and this is consistent with the purpose in view, for albumen is chiefly required at the earliest stage of the plant life; further, it is required only in small proportion, composing as it does only about 0.2 per cent of growing plants, and the young and more highly nitrogenous leaf is thus able to provide the necessary quantity for the matured leaf.

Other cultivated plants were then examined, and in every case organs showing the same essential characters were found, *viz.*, on turnip, rape, potato, beet, carrot, lettuce, chicory, tobacco, geranium, petunia, balm, daisy, and prunella. They were also found even upon representatives of plants having dense, hard, glossy leaves; for instance, they were found in profusion on the bud-leaves of a holly (*Holly laurifolia*), and of a species of pine (*Abies nigra*). These organs may conveniently be referred to as "albumen generators."

A remarkable confirmation of the soundness of the solution of the question was then got by finding its harmony with the experience of general practice and of scientific experiments. For it is found in general practice that the dicotyledons cultivated, and in particular legumes and turnips, though they contain a comparatively large quantity of nitrogen, require little nitrogenous manure, and are often retarded or injured by it, a fact that is now explained by the abundance of their albumen generators, which provide them with a sufficient quantity. On the other hand, the cultivated monocotyledons, such as cereals and grasses, though containing less nitrogen, urgently demand nitrogenous manures, and this is now fully explained by the comparative absence of "albumen generators." Thus, on barley, oats, and several grasses, at all stages of their growth, not a single albumen generator could be found, and the only available means of absorption, and that only to a small extent, appears to be the thin edge of the leaf in their youngest stage and the leaf-sheath.

It thus appears that all plants are able in various degrees to absorb the free nitrogen in air, and to transform it into albumen, by means of these specialised organs on their youngest leaves. This conclusion harmonises with scientific experiments, with practice, and with the natural growth of plants on the large scale, and thus presents a contrast to the many contradictions arising under the opposite doctrine.

Summing up:—Experimental chemical evidence has been given by Atwater's and Franck's trials that there is a gain of nitrogen in legumes bearing no nodules, the only source of which can be the air, and a smaller gain has been found by Franck in other plants.

Chemical evidence has been given by analyses which have shown that the leaves, deprived of their stalks, are richer in nitrogen than other parts of the plant, and that the youngest leaves bearing the albumen generators are fully one-third richer in nitrogen than the matured leaves.

Finally, biological evidence has been provided by microscopic examination. Thus there has been (a) pointed out an organ admirably situated and specially adapted for the absorption of nitrogen; (b) shown that this organ exists on all plants examined, including widely different families; (c) proved that these organs exist abundantly on highly nitrogenous plants, and sparsely on plants poor in nitrogen; (d) demonstrated that this organ is at first void

of, and becomes gradually gorged with, nitrogenous matter, and then disgorges the matter into the plant generally; (e) proved by recognised chemical tests that this matter is nitrogenous; and finally (f) shown that this solution of the problem conforms to the numerous results of experiments and to the experience of practice which were otherwise inexplicable.

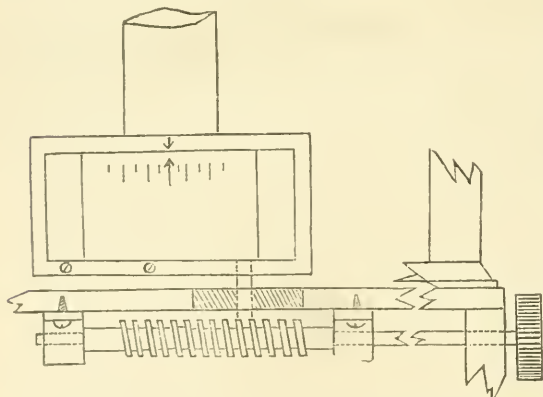
NEW SYSTEM OF ZERO FOR CHEMICAL BALANCES.

By JOHN McDOWALL, F.C.S.

BEFORE a balance is used for weighing the zero has to be taken, which is done by calculating the mean point on the scale through which the pointer moves. This method of taking the zero, although exact, is tedious, and requires much time, so much so that technical chemists to whom, as a rule, time is more valuable than extreme accuracy, usually set the pointer of the balance by means of the counterpoising screws at the centre of the scale every now and then, and work with that as zero, neglecting the small error that arises therefrom until it grows so great that the screws need re-adjusting.

It seemed that an improvement in this direction was desirable, and I have devised and tested an instrument by means of which the most sensitive balance can be set with perfect precision exactly in the centre of the scale in a few seconds without even opening the door of the balance case.

The ordinary ivory scale in the balance is replaced by a frame of brass, in which slides the scale in grooves in the frame as shown in the diagram.



The right-hand bottom corner of the scale is prolonged into a finger which goes through a slit in the side of the frame and then through another slit in the bottom of the balance.

The end of the finger is contracted into a tooth, and this engages with a screw, by the rotation of which the scale can be slid along the frame.

The rod of which the screw forms the centre is continued through a hole in the side of the balance and ends in a milled head similar to that used for releasing the pans.

The diameter of the screw spindle is made smaller about an inch from each end of the screw, so that the brackets which slip over it are arrested at the shoulder so that the spindle cannot move longitudinally and can only rotate.

When the milled head is revolved the screw rotates and moves the end of the finger along so that the graduated scale can be moved from one end of the frame to the other, the slits in the frame and bottom of balance being long enough for this purpose. Suppose now the balance has to be set at zero: the centre of the scale is set in the centre of

the frame and the pans are released, and after one or two preliminary swings the zero is taken.

Suppose the zero is a division or so to the left, the operator moves the scale through what he estimates to be a division by turning the milled head, and then takes another reading, using the eyes alone.

If the zero is still a little to the left he moves the scale on in that direction and takes another reading, and so on, until the pointer swings exactly the same number of divisions from each side of the centre line in the scale. The balance is now ready for use, and the operation has only taken a fraction of a minute.

When the pointer is several divisions out from the centre of frame the counterpoising screw may be given a turn so as to bring it roughly back to the centre, and then it can be finely adjusted by means of the sliding scale.

The instrument places in the hands of the technical chemist and assayer a means by which he can weigh as exactly as by the old method of calculating the zero, and no time is lost in the operation.

The balance on which the instrument was tested had a wooden bottom and a drawer, but it could easily be fixed to those having plate-glass bottoms; the slit in such a case would need to be ground out with a thin steel wheel and emery powder.

The instrument was made from my drawings by Becker and Co., and as the drawings are still in the possession of the firm there should be no difficulty in getting the article properly made, although the dimensions of the special balance would need to be given.

SOME DIETETIC PROBLEMS.*

By ROBERT HUTCHISON, M.D., F.R.C.P.

THE lecturer began by pointing out the great awakening of interest in Dietetic Problems which had taken place in recent years, and which had exhibited itself on the practical side in the promulgation of various systems of diet, more or less heterodox, for which their advocates claimed many advantages both economic and hygienic. With these systems the lecturer did not propose to deal, but rather to make clear the nature of the scientific problems which lie at the basis of the whole subject, and to which answers must be furnished before any acceptable system of practical dietetics could be formulated. In order to approach the subject in the clearest way some elementary preliminary matters had first to be considered. The two functions of food—(1) as a source of energy, and (2) as replacing waste—were therefore emphasised. Of the constituents of ordinary articles of food the proteids, carbohydrates, fats, water, and mineral matters, along with gelatin and alcohol, were alone of nutritive value, and in considering subsequent problems the first five of these need alone be taken into account. Emphasis was laid upon the fact that the proteids, mineral matters, and water are the nutritive ingredients which are concerned in replacing waste, whilst the proteids, carbohydrates, and fats are the chief energy-yielding constituents of the food. Reference was made to the large or kilo-calorie as the unit of energy employed in dietetics, and the caloric value of some typical foods was exhibited by the aid of a diagram. The lecturer then passed to the first of the problems which had to be considered, viz., how much energy (in calories) must the daily diet contain? It was pointed that a reply to this question might be arrived at (1) scientifically, by estimating the daily expenditure of energy in different forms by a subject confined in a respiration-calorimeter, or (2) empirically, by calculating the average amount of energy (in calories) contained in the freely chosen diets of a number of individuals doing a moderate amount of work, and whose weight was stationary. In this way such a balance sheet as the following could be constructed.

* A Discourse delivered at the Royal Institution, March 9, 1906.

Metabolic Balance Sheet (Man of 56 Kilos.).

Expenditure of Energy—

1. Internal work (heart, respiration, heat-production)	1550 cal.
2. Digestive work	240 "
3. External or muscular work—	
(a) Actual work done	250
(b) Increase under (1)	590
	840 "

Total 2630 "

Income as Food—

118 grms. proteid	484 "
56 " fat	521 "
500 " carbohydrates	2050 "

Total 3055 "

(Balance : 425 cal. = 45 grms. fat, or 2 ozs. adipose tissue.)

Attention being first confined to the expenditure side of the balance sheet, the nature of the outgoings of energy in each item under this heading was briefly explained. It was pointed out that the exact amount of energy expended under each head varied greatly in different circumstances and individuals.

1. The amount of "internal work" depended upon body-weight, the proportion of fat and muscle, the age, and most of all, upon the extent of body-surface. The latter factor was of the greatest importance as determining heat loss, and variations in the amount of energy consumed by different persons could be largely explained by it. This was illustrated by the fact that if we stated the amount of energy required at different ages in terms of body-surface, the results were surprisingly uniform.

2. The amount of the digestive work varied with the composition, and especially with the bulk of the food. The influence of bulk was so important that it had been calculated that if a horse were fed upon hay alone, 48 per cent of the energy in the hay was expended in its digestion.

3. The influence of external work upon expenditure required little explanation, but stress was laid upon the large increase which even slight degrees of work might entail. Thus, 12 per cent more of energy was expended when standing at attention than when standing at ease, whilst an hour's brisk walk increased the output of energy by 260 cal. Further, one must remember that any increase in external work increased also the expenditure under all the items classed as "internal work" as well. Apart from such variations as these, the question was raised whether there might not be individual variations in metabolism of which we are not yet able to give an exact account. Temperament, for example, was of importance, as determining the performance of superfluous movements, and in the rate at which muscular efforts took place. Apart from this, it was possible that some individuals might be "more economical machines" than others, producing, for instance, more work and less heat for a given supply of energy. The human body was certainly not a thermodynamic machine; it might be thermo-electric, chemico-electric, or chemico-dynamic, or even transform energy in some as yet unknown way, and so long as we were ignorant of its exact mode of working, the possibility of variations in the economy of the machine could not be absolutely denied.

Passing to the income side of the balance sheet, it was shown that this must be determined empirically, by a study of the composition of the diets actually consumed by persons of stationary weight under different conditions. A selection of the results yielded by such study was exhibited with the aid of a diagram, and from them the following "standard diet" had been deduced for a man of average weight, doing a moderate amount of work :—

Proteid	118 grms. =	484 cal.
Fat	56 " =	521 "
Carbohydrates	500 " =	2050 "

Total energy 3055 "

Assuming that the individual whose expenditure was studied in the above balance sheet was put upon such a diet as this, he would have a positive balance of 425 calories = 45 grms. fat, or 2 ozs. of adipose tissue daily. The question was raised whether this balance was necessarily stored as fat, or whether it might not circulate in the blood in some unknown form, and be broken down in abnormal ways giving rise to manifestations of disease. Upon the hypothesis that this could take place Dr. Francis Hare had founded his doctrine of Hyperpyraemia.

Assuming the standard diet above detailed to be that usually consumed, the further question arose, could not economy be effected? The lecturer suggested two directions in which this was possible :—(1) By a lessened heat production, (2) by a reduction of body weight. It was pointed out that in civilised conditions fat had ceased to be of value as a reserve of food, whilst the mere transport of several pounds of it entailed a considerable expenditure of energy. How much fat it was advisable to harbour in the body was an individual question to which no general reply could be given; it depended upon the "fighting weight" of the individual, *i.e.*, the weight at which his mental and physical efficiency was greatest.

Summing up, the lecturer pointed out that no definite reply could be given to the problem how much energy must be supplied in the daily ration owing to the great variations in expenditure above described. Empirical observation showed that 3000 calories was the average amount taken in, but the trend of scientific opinion was in favour of the view that this was perhaps needlessly liberal.

Turning to the second great problem underlying the science of dietetics—how much proteid is required daily in order to make good the daily waste of the body—the lecturer pointed out that it was impossible to construct a balance sheet for proteid in the body as could be done for energy, for the reason that the organism always tended to get into nitrogenous equilibrium on any quantity of proteid which was supplied up even to the limits of digestive capacity. It was shown by the aid of a diagram that, if an equal number of molecules of proteid, carbohydrate, and fat were brought into the neighbourhood of a cell, the cell did not break down equal proportions of each, but that the highest percentage of proteid molecules was destroyed; next in order of destructibility came carbohydrate, and last fat. This was probably due to the greater instability of the proteid and carbohydrate molecules, an instability which, in the case of sugar at all events, was the result of the presence in the molecule of an aldehyde or ketone group. If, on the other hand, a small number of proteid molecules and a relatively large number of those of carbohydrate and fat were brought simultaneously within reach of the cell, the mass influence of the more numerous molecules asserted itself, and, to use a simile, so distracted the attention of the cell that some of the proteid molecules escaped destruction. Hence the term "proteid spacers" as applied to carbohydrates and fats. It was pointed out that the theory of proteid spacers might furnish a reconciliation between apparently opposed systems of diet which yet seemed to give the same therapeutic results. It explained, for instance, how gout, which was presumably due to the presence in the blood of imperfectly oxidised proteid, might be treated successfully either upon a diet containing very little total proteid, or upon one in which the proteid spacers were largely excluded (*e.g.*, the "Salisbury" system). Another deduction which might be made from the theory was that it must always be easier to attain nitrogenous equilibrium upon a minimum supply of proteid if the latter was taken along with carbohydrates, so that both nutritive ingredients came under the action of the cells simultaneously.

Thus, to take most of the animal part of the diet at one meal and carbonaceous foods at others was wasteful of proteid, whereas a vegetarian diet in which carbohydrates and proteid are so intimately mixed that they reach the tissues at the same time, was that on which it was most easy to attain nitrogenous equilibrium on a relatively low proteid intake.

It followed also from the doctrine of proteid spacers that the amount of proteid necessary for the establishment of nitrogenous equilibrium must vary with the composition of the diet as a whole. It might be supposed that the nitrogenous output of fasting would provide an index of the proteid minimum. This, however, was found by experiment not to hold good, for proteid seemed so to stimulate the vital activity of all the tissues as to increase their power of oxidation; hence, if nitrogenous equilibrium is to be attained more proteid must be taken than is the equivalent of the nitrogen output of fasting.

The question for practical dietitians, however, was not what is the proteid minimum, but what is the proteid optimum? This question could only be solved empirically by observation of the amount of proteid actually consumed by persons in nitrogenous equilibrium. From such observations Voit had fixed the proteid optimum at 118 grms. daily. The lecturer then described the experiments of Chittenden, which seemed to show that health could be maintained on a much lower amount than this, even on as little as 60 grms. Did Nature furnish no hint as to the correct standard? It was suggested that in the proportion of proteid in human milk such guidance might be found. Assuming that an infant of six months consumed milk to the value of 578 calories daily, containing 14 grms. of proteid, and that the average energy-value of an adult diet was 3000 calories, it followed that if the adult was to take in the same proportion of his energy in the form of proteid as the child does, the standard for the adult would be about 74 grms. of proteid, it being further assumed that growth in the child might be set off against the greater wear and tear in the adult. The results of this method of attacking the problem were in striking harmony with those arrived at empirically by Chittenden.

The lecturer then touched upon the relative advantages and disadvantages of a low nitrogenous intake, emphasising the possible value of a proteid-rich diet in increasing the powers of resistance to infective disease, especially tuberculosis, and the danger of having no margin of circulating proteid to draw upon in case of emergency.

Summing up the reply to the second problem, it was shown that the proteid optimum must vary greatly in different circumstances and individuals, and in accordance with the composition of the diet as a whole, but that it probably stood nearer to the proteid minimum than had hitherto been supposed. The old and new dietary standards were then contrasted as regards both energy and proteid, and, in conclusion, the bearings of an acceptance of the new standard upon such practical systems of diet as vegetarianism were briefly indicated.

PREPARATION OF PURE ETHYL ALCOHOL.

By J. BISHOP TINGLE.

COMMERCIAL "absolute" alcohol always contains water, sometimes as much as 1 to 2 per cent; in addition to this, aldehyde is frequently present in varying quantity. The methods of purification in general use in laboratories, such as distillation over lime, baryta, sodium, &c., although adequate to remove the water, fail to affect the aldehyde, and it cannot be eliminated by fractionation. The problem of its removal has been attacked recently by L. W. Winkler in the following manner (*Ber.*, 1905, xxxviii., 3612):—Silver oxide, prepared from the nitrate, is well washed and dried at the ordinary temperature. It is then triturated with a little of the alcohol and the thin paste added to the remainder. The quantity of oxide used depends, of course, on the particular sample of alcohol; it need not exceed a few grms. to the litre, and may be less. To neutralise the acetic acid which is produced potassium hydroxide, 1 to 2 grms. per litre, is added; the mixture is frequently shaken and allowed to remain for several days at the ordinary

temperature, until a portion of the alcohol fails to give the test for aldehyde with ammoniacal silver solution.

The author recommends metallic calcium, in the form of filings, for the removal of water from alcohol; 20 grms. are usually sufficient to dehydrate 1 litre of commercial "absolute" alcohol. The substances are mixed, and boiled in a distillation flask with a reversed condenser, and then distilled; cork connections must not be used. The product is 99.9 per cent pure. A second treatment with 0.5 per cent of its weight of calcium appears to remove the last trace of water, because a third treatment, also with 0.5 per cent of calcium, was found to produce no further change. Certain physical properties of alcohol, purified in this manner and fractionally distilled, were determined with the following results:—Sp. gr. at 0° = 0.80629, at 10° = 0.79787, at 15° = 0.79363, at 20° = 0.78937; these figures are reduced to a vacuum, and referred to water at 4°. The corresponding values given by Mendeleeff are 0.80625, 0.79788, 0.79367, and 0.78945, respectively. The boiling-points are 77.81° (743.5 m.m.), 78.20° (754.9 m.m.), and 78.29° (757.8 m.m.); therefore a difference of 1 m.m. pressure causes a change of 0.034° in the boiling-point. The author mentions two rather curious facts which he has observed in the course of his work. The reaction between calcium and alcohol is the more vigorous the less water is present below 5 per cent, but ordinary alcohol, containing 5 to 10 per cent of water, also attacks calcium with considerable energy. Alcohol absolutely free from water is not nearly so hygroscopic as is usually supposed. For example, 200 c.c. of it were allowed to remain in an uncovered beaker, exposed to the air of the laboratory, during fifteen minutes; it was then found that the amount of water which had been absorbed was less than 0.1 per cent. —*American Chemical Journal*, xxxv., No. 3.

CORRESPONDENCE.

KIPP'S APPARATUS.

To the Editor of the Chemical News.

SIR,—In 1904 I described an improved form of Kipp's apparatus that I had devised and gave instructions for its use (*CHEMICAL NEWS*, vol. xc., p. 154). Apparatus thus made have now been in use in my laboratory for over two years without trouble, and with great increase of regularity and economy.

The object of this is to mention two points that have been observed during this time; these are:—

1. The apparatus can be moved about if ordinary care is used. The precaution of keeping it in one place which I suggested two years ago is not necessary.

2. Still further economy of acid can be effected if, when first charged, the space round the standing tube in Bulb 1 is also filled with spent solution as well as Bulb 3.

3. In using my apparatus for hydrogen, hydrochloric acid is preferable to sulphuric on account of the greater solubility of zinc chloride.—I am, &c.,

R. J. FRISWELL.

Laboratory, 43-45, Great Tower Street, London, E.C.
August 27th, 1906.

Variations of Electric Resistance of Steels at Temperatures removed from their Transformation-points.—P. Fournel.—The author has previously ascertained that the resistance of a steel varies in a different manner according as the temperature is above or below the region of the critical-point. He now finds that the electric resistance of a steel increases at first according to a linear law, and then, at a temperature depending on the composition of the metal, the curve rises and becomes parabolic.—*Comptes Rendus*, cxliii., No. 5.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii, No. 5, July 30, 1906.

Compounds of Ammonia with Chloride, Bromide, and Iodide of Gold.—Fernand Meyer.—The author investigates the action of dry ammonia (both liquid and gaseous) on the halo-aurous compounds. He thus prepares the compounds $\text{AuI} \cdot 6\text{NH}_3$ and $\text{AuBr} \cdot 2\text{NH}_3$. When liquid ammonia acts on aurous chloride a white paste is formed, very slightly soluble in the liquid. At -28° , after the excess of ammonia has evaporated, the product obtained corresponds to the formula $\text{AuCl} \cdot 12\text{NH}_3$.

Some Reactions of Liquid Chlorine.—V. Thomas and P. Dupuis.—When liquid chlorine acts on iodine a brisk reaction takes place, the trichloride of iodine being produced. The reaction of chlorine on bromine at a low temperature is the same as on iodine. However, when the temperature is raised a decomposition takes place and excess of chlorine is given off, leaving the residue BrCl . When liquid chlorine acts on sulphur, selenium, and their compounds, bodies of the type MCl_4 are produced. On arsenic, antimony, bismuth, and gold the same reaction takes place, but not so easily.

Alloys of Manganese and Molybdenum.—M. Arrivant.—The author prepares alloys of manganese and molybdenum, and finds that when these bodies contain less than 30 per cent of molybdenum they consist of free manganese associated with one of the constituents, Mn_6Mo or Mn_4Mo . These two latter can be isolated by a careful treatment of the alloy with dilute acetic acid.

Estimation of Ammonia in Water by Nessler's Reaction.—Albert Buisson.—The author investigates Nessler's reaction for the estimation of ammonia in water, and finds that the reaction is not total, but a state of equilibrium is established between the different elements present. The estimation of ammonia in water, effected by the estimation of the mercury in the precipitate, is inexact, the total ammonia not being precipitated, and the composition of the precipitate not being estimable by any known law. The colorimetric method is acknowledged to be empirical—a portion only of the ammonia sufficing to give the coloration which is the basis of the estimation.

The Crystalline L-Idite of Synthesis.—Gabriel Bertrand and A. Lanzenberg.—The substance which E. Fischer called *d*-idite, M. Bertrand has found to be identical with sorbierite. The authors now use Fischer and Fay's method, and simplify it by transforming the xylose into a mixture of *l*-gulonic and *l*-idonic acids, and, instead of purifying this latter by brucine salts, they make the gulonic lactone crystallise out and treat the mother-liquor directly with sodium amalgam. They thus prepare *l*-idite accompanied by a little *l*-sorbite, but the latter can be eliminated in part by passing it through benzoic acetal. The *l*-idite, after purification, has the composition $\text{C}_6\text{H}_{14}\text{O}_6$.

Silver Sulphide, Selenide, and Telluride.—H. Pélabon.—The author investigates the curves of fusibility of mixtures obtained by melting silver with sulphur, selenium, and tellurium. In all cases the ordinates are the values of the temperature of the beginning of solidification, and abscissæ the value of the proportion, R, of the weight of silver to the total weight of the mixture.

Washing of Colloidal Precipitates.—J. Duclaux.—There has always been a considerable analytical error due to the difficulty of washing colloidal precipitates, such as $\text{Fe}_2(\text{OH})_6$. The author investigates the matter, and finds that the theory in the case of the iron precipitate, that the ultimate mixture is $\text{Fe}_2(\text{OH})_{6.1\frac{1}{2}}\text{Fe}_2\text{Cl}_6$, and that, when

this composition is reached, no amount of washing will remove any more chloride, is not strictly true. In reality, an equilibrium is established between the chlorine in the colloid and in the intermolecular liquid. He effects a separation of the two parts of the colloid by filtration through collodion, and analyses each. He thus obtains a limit of washing corresponding to the formula $\text{Fe}_2(\text{OH})_{6.4\frac{1}{2}}\text{Fe}_2\text{Cl}_6$.

MISCELLANEOUS.

Additional Notes to Mr. F. Soddy's Paper on "The Evolution of the Elements" (Aug. 24).—At p. 88, col. 2, after line 21, insert—

"This indicates that thorium is not a member of the uranium-radium series, for in this case there would exist no proportionality between the uranium and radium, although there would be between the thorium and radium."

After line 38, insert—

"In the subsequent discussion opened by Mr. Strutt on the connection between radium and the internal heat of the earth, the author suggested that Strutt's results seemed to offer the first experimental indication that such a process of atomic upbuilding with absorption of energy was taking place in Nature."

The following corrections should also be made:—P. 85, col. 1, line 23, for "distinctive" read "destructive." Col. 2, line 12, for "*ἐν το πᾶν*" read "*ἐν το πᾶν*."

Attempt on the Life of Prof. Harrison, C.M.G., M.A.—The news has lately come to hand of an attempt to bar the progress of the practical application of scientific knowledge in such a manner as to call for some comment. A certain section of the Creole inhabitants of Georgetown, British Guiana, have apparently a keen sense of poetic justice, and a firm belief in the efficacy of meeting the devil with his own weapons. So when the Director of the Government Laboratory made inconvenient discoveries relating to the adulteration of foods and the illicit distillation of spirits, they felt that a scientific method of retaliation would meet the case, and proceeded to arrange for the addition of large quantities of arsenic to the supply of drinking-water in the laboratory. The results of this scheme, although no doubt disappointing to its originators, were sufficiently serious. Prof. Harrison, the Director of Science and Agriculture in British Guiana, was rendered dangerously ill, and has had to be invalided home in consequence to recuperate, and no fewer than seven of the assistant analysts and others who drank the water were affected, so that the laboratory actually had to be closed for one day owing to the indisposition of the whole staff. We are glad to take this opportunity of expressing our sympathy with Prof. Harrison, who was the chief sufferer, and the hope that he may soon be completely restored to health. Although in more enlightened countries the methods of disposing of unpopular officials are perhaps a trifle more subtle, instances are not wanting to show that merit and distinction in the scientific world are by no means always recognised at their true value, and there is all the more food for thought in this reflection, because the would-be obstructors of the progress of science are not, as in British Guiana, the uneducated, who regard it merely as providing an arbitrary method of reducing profits, but those to whom the administration and guidance of the affairs of the nations are entrusted.

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UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following five subjects:—(1) English—Composition, Précis Writing, salient facts in English History and Geography. (2) Elementary Mathematics. (3) Latin or Elementary Mechanics, or Elementary Physics—Heat, Light, and Sound, or Elementary Chemistry, or Elementary Botany. (4) and (5) Two of the following subjects, neither of which has already been taken under Section (3). If Latin be not taken, one of the other subjects selected must be another Language from the List, either ancient or modern:—Latin, Greek, French, German, *Arabic, *Sanskrit, *Spanish, *Portuguese, *Italian, *Hebrew, and *Zoology, Ancient History, Modern History, Logic, Physical and General Geography, Geometrical and Mechanical Drawing, Mathematics (more advanced), Elementary Mechanics, Elementary Chemistry, Elementary Physics—Heat, Light, and Sound, Elementary Physics—Electricity and Magnetism, and Botany. Candidates in subjects marked with asterisk must give at least two months' notice before the commencement of the Examination.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Several valuable Scholarships and Exhibitions are available to students.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry candidates are required to show a general acquaintance with General Theoretical Chemistry, Chemistry of Carbon Compounds, Physical Chemistry, and History of Chemistry since the time of Boyle.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

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This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S. *Lees Reader in Chemistry*—G. Brereton Baker, M.A.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. Watts, M.A., and J. E. Marsh, M.A.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S. *Jacksonian Professor of Natural and Experimental Philosophy*—Sir James Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open

daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

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Demonstrator—W. C. Ramsden, F.C.S.

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The Laboratories and the Lectures of the Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

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2. *Organic Chemistry*.—General, second year; advanced, third year.
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The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

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Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the pro-

cesses of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *visà voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry: Winter Session, £5 5s.; Summer Session, £3 3s. Practical Chemistry: Winter Session, £5 8s.; Summer Session, £4 4s. Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; One Term, £10 10s.; Two Terms, £18 18s.; Three Terms, £26 5s. Three days a week: One month, £2 12s. 6d.; One Term, £6 6s.; Two Terms, £11 11s.; Three Terms, £15 15s.

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In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

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Classes for Evening Instruction in various subjects are held during the Winter Session.

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Assistants—E. C. C. Baly, F.I.C.; J. K. H. Inglis, D.Sc., M.A.; N. T. M. Wilsmore, M.Sc.; and S. Smiles D.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 3 to December 21; Second Term, from January 15 to March 27; Third Term, from April 23 to July 8.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Friday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a

week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

In this Course the physical principles bearing on Chemistry are first discussed, and the Chemistry of the Elements and their compounds is treated in considerable detail, under the headings—Elements; hydrides, halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

Fees: Course, £7 7s.; First or Second Terms, £4 4s. A Practical Class will meet throughout the Session.

Course of Physical Chemistry.

October to February: Tuesday and Thursday at 9. February to June: Monday and Saturday at 9.

The Principles of Chemistry will be specially considered, comprising the Atomic Theory, Chemical Classification, the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent Chemical Theory researches.

Fees:—Courses, £5 5s.; Term, £2 2s.; for a second course, £1 1s.

Senior Course of Inorganic Chemistry.

This Course will begin about the middle of February; Tuesday and Thursday at 9. Fee, £3 3s.

Electro-chemistry.

First Term, Monday and Saturday at 9; Second Term, Wednesday and Friday at 12. Fee, £2 2s.

Organic Chemistry.

Mon. at 12, Wed. and Fri. at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the Course of Physical Chemistry, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.] for a Second Course, £3 3s.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

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Assistant Professor—M. O. Forster, Ph.D., D.Sc.

Demonstrators—H. Chapman Jones; G. T. Morgan, D.Sc., A.R.C.S.; and J. C. Philip, M.A., Ph.D., B.Sc.

Assistants—G. S. Newth and Miss Whiteley, D.Sc., A.R.C.S.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Board of Education. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction lasts for three years, is the same for all the divisions during the first year, after which it is specialised according to the particular division in which the student is working for the Associateship.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject except Mining and Metallurgy and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	£ 5	£ 13
Physics	3	12
Biology with Botany	5	12
Geology with Mineralogy	4	8
Mechanics	4	6
Metallurgy	4	13
Mining	2	4

The fee for the course of Mine Surveying is £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

The Session is divided into two Terms. The first Term begins about the first week of October, and ends about the middle of February. The second Term begins in the middle of February, and ends about the middle of June.

The hours of study are from 10 a.m. to 1.15, and from 2 to 4 or 5 p.m. every day, except on Wednesday and Saturday, when the College closes at 1 p.m.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of in-

struction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixty-fifth Session will commence on Oct. 1, 1906.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C. (Dean); Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. UNIVERSITY OF WALES.

Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Assistant Lecturers and Demonstrators—A. Brooke, Ph.D. (Strass.), and T. C. James, M.A. (Cantab.), B.Sc.

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

Lecturer on Dyeing—(Vacant).

The College is open to male and female students above the age of sixteen years. The Session commences on Oct. 2nd, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1906-1907, Course B). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction

necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 18, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturer and Demonstrator, Alice E. Smith, B.Sc. Assistant Lecturer in Agricultural Chemistry, Alan Baguley, B.Sc., F.I.C. Junior Demonstrator, J. O. Hughes, B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 4th, 1906. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Inorganic and Physical Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Demonstrator—R. D. Abell, D.Sc.

Lecturer in Metallurgy—A. A. Read, F.I.C., F.C.S.

The Session commences October 9th, and terminates on June 28th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Inorganic Chemistry; Fee, £3 3s.

A short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Morris W. Travers, D.Sc., F.R.S.

Assistant Professor—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturer—Oliver C. M. Davis, B.Sc., A.I.C.

Lecture Assistant—J. H. Sturgess.

The session 1906-1907 will begin on October 2. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering

and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Registrar.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Elementary Course.—Three Lectures a week will be given during the Session. Fee, £3 13s. 6d.

Special Course.—A special course of Lectures is also given to Elementary Teachers.

General Course.—Four Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Advanced Course.—Two Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Organic Chemistry.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d. An advanced course of lectures will also be given one day a week during the session. Fee, £2 2s.

Practical Chemistry.—Laboratory Instruction.

The Chemical and Metallurgical Laboratories will be open daily from 9 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

Days per Week ..	Five.	Four.	Three.	Two.	One.
Per Session	15	12½	10	7½	5
„ Two Terms	11	9	7½	5½	3½
„ One Term	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

EVENING LECTURES.

A course of Lectures, which is subject to variation to suit the requirements of Students, will be delivered during the Session. Fee, 10s.

Pharmaceutics.—During the second and third Terms a course of Lectures will be given one evening a week dealing with the recent advances in Chemistry. Fee, 5s.

Practical Chemistry.—Laboratory Instruction.—The Laboratory will be open one evening a week from 6 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—Two Terms, 21s; One Term, 12s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Registrar.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY AND METALLURGY.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.
Assistant Professor—G. P. Darnell Smith, B.Sc., F.I.C., F.C.S.

Lecturers—H. A. M. Borland, A.R.C.S.; E. E. Elt, B.Sc.
Demonstrators—E. H. T. Parker; P. W. Alloway;
C. D. Fuller.

Assistants in Chemical Laboratory—W. F. Phillips and C. Cox.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry, Analysis, and Assaying, to Students of either sex. They include the Junior Laboratory (for forty Students working at one time), Senior Laboratory, Balance Room, Combustion Room, Store Rooms, Metallurgical Laboratory, and Research Laboratory. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying.

Special facilities will be given to Students wishing to undertake research work approved by the Professor; and the Courses provide for the Examinations in Chemistry for the B.Sc., M.B., and D.Sc. degrees of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute.

Certificates of Proficiency in Assaying will be given to Students who complete a Course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College examinations in the Theory and Practice of Assaying.

The Laboratories are open every week-day from 9 till 12 noon, and from 1.30 to 4.30 p.m., except Saturday, when they close at noon.

The Annual Fee of £10 10s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop.

The College Day Classes re-open on Sept. 18, and the Evening Classes commence on Monday, October 1.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (free).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S., P.I.C.

Assistant Lecturers and Demonstrators—Alex. Findlay, M.A., D.Sc., Ph.D.; Hamilton McCombie, M.A., Ph.D., B.Sc., A.R.C.S., A.I.C.; C. K. Tinkler, B.Sc., and T. J. Murray, Ph.D.

The Session will be opened on October 1st, 1906.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. Mondays to Thursdays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon

Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—*Advanced Organic Chemistry.*—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *General and Physical Chemistry.*—This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General and Physical Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term . .	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

DEPARTMENT OF CHEMISTRY AND DYEING.

Head of Department—Prof. W. M. Gardner, M.Sc.

Lecturers in Chemistry—B. North, A.R.C.Sc. (Lond.)
L. L. Lloyd, Ph.D.; S. F. Stell, F.C.S.

Demonstrator in Chemistry—S. R. Illingworth.

Lecturer in Physics—J. A. Tomkins, A.R.C.Sc. (Lond.).

Demonstrator in Physics—E. B. Walker.

Lecturers in Dyeing—A. Herz, Ph.D., and A. B. Knaggs, F.C.S.

Demonstrator in Dyeing—L. Minikin.

Lecturer in Gas Manufacture—W. Cranfield.

Lecturer on Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

I. *General Chemistry Course*, extending over four years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Extending over one or two years.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.)*, London.—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on three half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc.

Lecturer on Physical Chemistry—H. M. Dawson, B.Sc., Ph.D.

Assistant Lecturers and Demonstrators—C. E. Whiteley, M.Sc., and W. Lowson, B.Sc., F.I.C.

Demonstrator—W. H. Perkins, B.Sc.

The Session begins October 1, 1906.

Lecture Courses.

1. *General Course of Chemistry*.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. *Advanced Inorganic Chemistry*.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. *Advanced Inorganic Chemistry*.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.

4. *Organic Chemistry*.—Tuesday, Thursday, and Saturday at 12 noon. Fee £3 13s. 6d.

5. *Honours Courses*.—(a) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon in the First and Second Terms; fee, £2 12s. 6d. (b) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £1 11s. 6d. (c) Physical Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the Second and Third Terms; fee, £2 12s. 6d. (d) Electro-chemistry: One hour weekly; 31s. 6d.

6. *Chemistry of Food and Drugs*.—Special class for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £2 2s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from April to June. Fee, £5 5s.

Elementary Science for Teachers.—Saturdays, 9.30 to 12.30, for half the session. £2 12s. 6d.

Dyeing and Tintorial Chemistry Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Assistant—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—A. B. Steven, B.Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, M.Sc., F.I.C.

Assistant Lecturer and Demonstrator—F. Kopecky.

Demonstrator—Harold Brumwell.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, viz., the Salt, Akroyd, Brown, Baines, Emsley, Craven, Wheatley, Leeds City Council, and Clothworkers' Scholarships, and one of the 185 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Chemistry—J. Campbell Brown, D.Sc.

Professor of Physical Chemistry—F. G. Donnan, M.A., Ph.D.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—Gay D. Ricketts, M.A.

Demonstrators and Assistant Lecturers—A. T. de Moulpied, M.Sc., Ph.D.; H. Bassett, B.Sc., Ph.D., D.es.Sc.; F. J. Brislée, D.Sc.; J. McConnan, M.Sc., Ph.D.; A. Rule, M.Sc., Ph.D.; and E. Garratt, M.Sc.

Assistant—H. H. Froyssell.

The Session commences October 9th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £3.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £3.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £3.

Course F.—Physical Chemistry. Fee, £2 10s.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—History of Chemistry and Chemical Philosophy. Fee, £2.

Courses J.—Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Fuel and Gas. (6) Technical Gas Analysis.

Course K.—Applied Organic Chemistry.

Course L.—Applied Electro-chemistry.

Fee (Courses J, K, L), three terms, £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances; preparation of Inorganic Compounds. (3) Revision Class. (4) Engineers' Class. (5) General Metallurgy (Elementary).

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water and Gas Analysis, Photometry and Photography, Electro-chemical Work, Metallurgy Laboratories, Research Laboratories and Library, and a Museum. Large new Laboratories for Physical Chemistry and Electro-chemistry have been recently erected, and will be opened October 13th.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

D.P.H. Course (see special syllabus).

Course for Dental Degree (see special syllabus).

Veterinary Course (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1906, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held during the winter.

Prospectuses containing particulars may be obtained from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE

Professor of Chemistry—P. Phillips Bedson, M.A. D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—F. C. Garrett, D.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturer and Demonstrator—J. A. Smythe, M.Sc., Ph.D.

Demonstrator—A. A. Hall, M.Sc., Ph.D.

First Year Courses.—I. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 4th. Fee, £3 10s. for the Session.

II. *Special Course.*—More advanced than the above. Wednesdays and Fridays, 11 to 12. Fee, £3 10s. for Session.

For Diploma in Electrical Engineering.—Tuesday, 12 to 1. A course of Lectures will be given dealing with the Principles of Chemistry, Fuel, the Phenomena of Combustion, and Metals and Alloys employed in Engineering, &c. Fee for the course, £2.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 3rd. The class for Inorganic Chemistry meets at 11 a.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Professor Louis, M.A., F.I.C., F.C.S.; Demonstrator, H. Dean, A.R.C.M. A Metallurgical Laboratory is provided, in which instruc-

tion is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. **Laboratory Fees.**—Students working two days, £3 10s. per term, £9 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in the following subjects:—Arithmetic; English Essay; Geometry; the subject-matter of Euclid, Books I., II., III.; Algebra, up to and including Quadratic Equations. Also any two of the following:—English Language; Latin, including Grammar and Easy Sentences; Greek; French; German; Geography. The next examination commences on September 24. Names to be sent in at least ten days before this date. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—1. The first examination for the Degree of B.Litt. 2. Durham Examination for certificate of proficiency in General Education, held in March and September. 3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

The University has recently adopted a Matriculation Examination for students entering the Faculty of Science, particulars of which can be obtained from the Secretary.

Bachelorship in Science.—Every candidate for the Bachelorship in Science will be required to satisfy the examiners in Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the third year in an examination in one chief and two auxiliary subjects. For details of the subjects the College Calendar should be consulted. Candidates may qualify for the degree of B.Sc. by attending special courses in Agriculture, Engineering, and Mining, and passing the several examinations.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in September next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 25th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing October 1st. Candidates should send in their names to the Secretary on or before September 20th.

THE UNIVERSITY OF MANCHESTER.

Professor and Director of the Chemical Laboratories—Harold B. Dixon, M.A., M.Sc., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Lecturers and Demonstrators—G. H. Bailey, D.Sc., Ph.D.; D. L. Chapman, B.A.; Norman Smith, M.Sc.

Assistant Lecturers and Demonstrators—E. C. Edgar, D.Sc.; C. Weizmann, Ph.D.; H. F. Coward, M.Sc.; Ida Smedley, D.Sc.

Lecturer in Organic Chemistry—J. F. Thorpe, Ph.D.

Professor of Metallurgy—H. C. Carpenter, M.A., Ph.D.

Lecturer in Electro-Chemistry—R. S. Hutton, D.Sc.

The Session begins October 2, 1906.

The Chemical Classes form part of the Courses for Degrees in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during the Lent Term.

These courses are intended for Students commencing the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: Two hours per week during the Michaelmas Term.

Applied Electro-chemistry.—One hour per week during Lent and Easter Terms. A course of six lectures on the Electric Furnace and its Applications will be given on Saturday afternoons during the Michaelmas Term.

Applied Chemistry.—(1). Sulphuric Acid and Alkali Manufactures; General Principles of Chemical Engineering. (2). The Natural and Artificial Colouring Matters and the Principles of Dyeing and Printing. (3). The Chemistry of Fuel.

Chemistry Laboratory Courses.

During the first year, the student works in the "Roscoe" or the "Dalton" Laboratory at Qualitative Analysis and Inorganic Preparations. Second Year Students work at Quantitative Analysis, and also take a Laboratory Course in Physics or some other subject. Third Year Students work in the "Schorlemmer" Laboratory of Organic Chemistry, and may also undertake experimental work in some special branch of Chemistry.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Metallurgical Laboratory.—This has been recently much enlarged and re-equipped, mainly with a view to post-graduate work on the Structure of Metals and the Chemistry of Fuel.

Applied Organic Chemistry.—In connection with the "Schorlemmer" and "Schunck" Laboratories, a special laboratory is fitted with apparatus and appliances suitable for investigations on Dyes and other organic substances on a large scale.

Electro-chemical Laboratory.—In addition to such apparatus as is required for experimental work on Electrolysis

and the Electro-deposition of Metals, special equipment is provided for investigations with the Electric Furnace.

Chemical Research.

In addition to the facilities mentioned above for Metallurgical and Electro-chemical Research, the following laboratories are available for post-graduate work:—(1) The Private Laboratories of the two Professors; (2) The "Frankland" Laboratories for Physical Chemistry; (3) The "Schunck" Laboratory for Organic Chemistry; (4) The "Thorpe" Laboratory for Organic Chemistry.

To encourage post-graduate work of this kind the University gives a "Beyer" Fellowship (£100 per annum) and Scholarships (£50 per annum).

The "Dalton" Chemical Scholarship (£50 per annum, tenable for two years) is also awarded, and the 1851 Exhibition Scholarships (£150) may be held in the Laboratory. Further, Honorary Research Fellowships and Research Studentships are granted from time to time to those who are capable of carrying out original investigations.

Two "Schunck" Research Assistants are appointed annually.

Courses for Degrees.

To qualify for the Ordinary Degree of B.Sc. Students have to attend a prescribed course of study extending over three years, and are recommended to pass the Matriculation Examination before entrance. (Subsequent to October, 1906, three years attendance after matriculation will be compulsory).

The course of the Degree of B.Sc. with Honours in Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); an additional course (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Physical or some other Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Lecture course in some Special Branch of Chemistry; History of Chemistry; Chemical Laboratory (5 days per week, for one of which attendance in another Laboratory may be substituted).

For the M.Sc. Degree post-graduate work is required. The D.Sc. may be obtained after four years from graduation, provided that the candidate has distinguished himself in research.

Certificate in Applied Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. Sand, Ph.D., M.Sc.; and R. E. Rose, Ph.D.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences October 1st, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these

lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S. *Lecturers and Demonstrators*—A. N. Meldrum, D.Sc.; W. E. S. Turner, M.Sc., B.Sc.; W. J. Jarrard, B.Sc.

The Session will commence October 3rd.

Matriculation Course.—Tuesday and Friday at 9.30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Intermediate Course for B.Sc. or M.B.—Monday and Thursday at 9.30 a.m.; Tuesday and Friday at 10.30 a.m. £4 4s. and nine hours per week Laboratory work.

B.Sc. Course.—Monday and Wednesday, and another hour to be arranged, £4 4s., and twelve hours per week Laboratory work during two Sessions.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.

Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health will be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Board

of Education, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lecture Class and Laboratory, on Wednesday evening during the Michaelmas and Lent terms. Fee, £1 10s.

DEPARTMENT OF METALLURGY.

Professor of Metallurgy—J. O. Arnold. This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A new steel works has recently been erected in connection with the Sheffield College at a cost of about £10,000. The works include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works are also provided with a hammer capable of dealing with four-inch ingots. Differential annealing furnaces, oil brightening and lead-tempering tanks will constitute part of the new plant. Additional laboratory accommodation is attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers—J. S. Lumsden, Ph.D., D.Sc., and J. K. Wood, D.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins early in October and ends in March. The Summer Session extends from the middle of April to the end of June.

The *Junior Lecture Course on Systematic Chemistry* is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—Francis W. Gray, M.A., B.Sc., and John Alexander, M.A., B.Sc.

I. General Lecture Course (100 Lectures).—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. Special Lecture Course on Organic Chemistry (50 Lectures).—Daily during the Summer Session. Fee, £3 3s.

III. Practical Course for Medical Students.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £4 4s.

IV. Chemical Laboratory.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. Fee, £4 4s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

V. Physical and Advanced Inorganic Chemistry (30 Lectures).—In connection with the Laboratory work, three Lectures a week on Physical Chemistry and selected portions of Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Mr. F. W. Gray. Fee, £2 2s.

UNIVERSITY OF ABERDEEN AND ABERDEEN AND NORTH OF SCOTLAND COLLEGE OF AGRICULTURE.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; W. J. Profeit, M.A., B.Sc.; and H. M. Will M.A., B.Sc.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. Agricultural Chemistry (General Course).—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. Laboratory.—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; and W. W. Taylor, M.A., D.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee, £4 4s. Advanced Courses of 25 lectures each are given in the Winter and Summer Sessions; fee, £1 1s. An Intermediate Course of Organic and Advanced Inorganic Chemistry is held in summer; fee, £2 2s. There is also a class on History of Chemistry or Chemical Theory, by Dr. Dobbin; fee, £1 1s.; and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis), Physico-chemical Measurements, Agricultural Chemistry, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical Chemistry; Organic Chemistry; Physical Chemistry;

Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by himself:—Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—R. B. Denison, M.Sc., Ph.D.; Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.; E. B. R. Prideaux, M.A., D.Sc.

The Session begins October 2nd, 1906.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electro-chemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Students who have been three and four years in the Chemistry Department, arrangements have been made for their spending from four to twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory, under the charge of Dr. Emil Westergaard, has been provided for the study of Technical Mycology, including Brewing, Distilling, Maling, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Bread Making, Butter and Cheese Manufacture, &c.

Matriculation Fee, 5s.; Composition Fees from £12 12s. to £15 15s. Full particulars are published in the Calendar of the College, which is issued early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.

Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.

Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 25. Entrance Examination Sept. 17. The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts,

Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1906-1907 may be had from Mr. H. F. Stockdale, Secretary; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry—T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 15th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for forty Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 28th and following days. Twenty-one of these Bursaries are restricted to Men, two to Men or Women, and fourteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candi-

dates for the Examinations in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £5 5s.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity of conducting chemical investigation.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years, 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—John Hawthorne, Ph.D., F.C.S.

The College Session will commence on October 16th, 1906, and end on June 8th, 1907. All classes are open to male and female students.

The courses in Chemistry, though designed primarily to meet the requirements of candidates proceeding to the Examinations in Arts, Medicine, and Engineering of the Royal University of Ireland, of the Medical Licensing Bodies of Dublin and Edinburgh, and of the Pharmaceutical Society of Ireland, can be arranged specially as required, so as to render them suitable to any particular course of study. The following courses are provided:—

Systematic Chemistry.

I. General Lecture Course; three terms. Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.

II. Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.

III. Winter Course of Practical Analytical Chemistry; commencing early in January, 1907.

IV. Summer Course of three months' duration, for students of Medicine; ending about the third week in June.

V. Course for Pharmaceutical Students; held during the second and third terms.

Laboratory Work.

VI. The Chemical Laboratory is open daily from 10 to 4 o'clock, except on Saturdays, to Students entering for Special Courses of practical work in General Inorganic Chemistry, Qualitative and Quantitative Analysis, Organic Chemistry, or for the purpose of Original Investigation.

Scholarships, &c.—In addition to the Class Prizes given at the Sessional Examinations, the College awards a Senior Scholarship of the value of £40, for Chemistry and Physics (either of which may be taken as a limited course), and numerous Junior Scholarships in Arts, Medicine, and Engineering, of which chemistry forms a part, value from £20 to £24 each, annually. The Royal University of Ireland also offers Exhibitions in Chemistry and Physics, First-class value £42, and Second-class value £21, together with other prizes, e.g., a Studentship of £100 per annum, tenable for three years; and the 1851 Exhibition Scholarships, value £150, tenable for two, and, under certain circumstances, for three years, have from time to time been placed at the disposal of the College.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., F.I.C., F.C.S.

Demonstrator—Miss Rosalind Clarke, B.A.

Research Assistants—W. Sloan Mills, M.A., B.E., and Percy C. Austin, M.A.

The Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and Organic, and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by four Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Dean of Faculty and Professor of Chemistry—W. N. Hartley, F.R.S., D.Sc.

Lecturer on Organic Chemistry—Alphonsus O'Farrelly, M.A.

Senior Assistant—J. Holms Pollok, D.Sc.

Junior Assistant—G. G. Leonard, A.R.C.Sc.I.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships include free education for the full Associateship Course of three years and maintenance allowance of a guinea a week during the Session.

CHEMICAL LECTURES, CLASSES, AND
LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds Central Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 18th, and

the Winter Session opens on Tuesday, October 2nd. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 18th. Session begins October 2nd. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—I. S. Scart, F.I.C., F.C.S., and Assistants. Courses of Saturday and Evening Lectures and Laboratory Practice in Chemistry and Physics, open to Students of both sexes. Day Commercial School, commences Sept. 17. Session commences October 1st.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells, Wh.Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), assisted by Mr. John L. White, D.Sc., Mr. H. Evans, and others. Session opens Sept. 24. Complete courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Paper and Pulp Testing, Paper Making, Gas Analysis, Assaying, Oils, Fats, Soaps, and Candles.

BIRKBECK COLLEGE, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. Alex. McKenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. This Institution, which has now completed eighty-three years of educational work, will commence the new Session on Wednesday, September 26, when Sir Edward Busk, Vice-chancellor of the University of London, will give the Opening Address, at 7.30 p.m. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Law, and Logic. Courses conducted by recognised teachers of the University provide for the Examinations of the University of London, in the faculties of Arts, Science, Commerce, and Law. The Report for the last session shows that during the year 65 students passed some University examinations, while a large number gained successes at various public examinations. The College has added considerably to its appliances in recent years, and the Physical, Chemical, Biological, and Metallurgical laboratories are very thoroughly equipped. Courses in Mining, Metallurgy, and Assaying are given both in the day and evening. The Modern Language classes include Italian, Spanish, as well as French and German. The College has a School of Art, open both day and evening. Good Reading and Magazine Rooms are provided. The Calendar supplies detailed information respecting the Courses of Study, Examinations, Studentships, &c. A popular Lecture or Entertainment is given in the Theatre every Wednesday evening from October to April.

BRIXTON SCHOOL OF CHEMISTRY AND PHARMACY, 171, Brixton Road, London.—Principal, Dr. A. B. Griffiths, F.R.S.(Ed.). Lectures on Inorganic and Organic Chemistry, Physics, Botany, &c., for Pharmaceutical, Medical,

and other students. The benches in the laboratory are fitted with every convenience. There are courses in Research Work. Full particulars as to fees, &c., may be obtained by writing to the Principal.

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road, S.E.—Chemistry: Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry (Session fees, per course, 10s. to 20s.). Day Practical class in Electro-chemistry, lecture on Friday evenings. Special Saturday Morning Class in Practical Chemistry (10s.); Dr. F. Mollwo Perkin, assisted by H. D. Law, B.Sc. Electricity and Magnetism, and Electro-technics: Evening Lectures and Laboratory Work (Session fees, per course, 10s. to 30s.), Dr. J. Henderson, assisted by H. Saunders. Special Evening Courses on Painter's Oils, Colours, and Varnishes. Special Day Courses in Technical Chemistry and Electro chemistry (October to July), £10. Session opens Monday, Sept. 24.

SOUTH WESTERN POLYTECHNIC, Chelsea, S.W.—Principal, Sidney Skinner, M.A. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, Photography, &c. Systematic Courses are held for the Matriculation, Intermediate Science, and B.Sc. Examinations of the University of London. The Day Course in Chemistry is of three years' duration; it gives a thorough training to those who wish to become Consulting or Industrial Chemists. Prospectus of Day and Evening Classes may be obtained from the Secretary, 1d., by post 4d.

EAST LONDON COLLEGE, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Assistants, Clarence Smith, D.Sc., and F. G. Pope, B.Sc. Lectures and Practical Classes are conducted in the Day Technical College, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination, B.Sc. (Honours and Pass). Special attention is given to work for the Honours Examination and research. Evening Classes for London University Degrees are also held. The College re-opens October 1st.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate.—Principal, Charles A. Keane, M.Sc., Ph.D., &c., assisted by H. Burrows, Ph.D., F.I.C., Arthur R. Ling, F.I.C., R. S. Willows, D.Sc., and C. O. Bannister, A.R.S.M. Evening Classes in Chemistry, Metallurgy, Brewing and Malting, Physics, and Mathematics, designed to meet the requirements of those engaged in Chemical, Metallurgical, and Electrical industries, and also in other departments of Science and Art. Practical laboratory work. Courses of Instruction in Glass Blowing, by A. C. Cossor. Classes begin September 24. Full details may be obtained on application, or by letter to the Principal.

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, (i.) to promote the better education of persons desirous of becoming public and technical analysts and chemical advisers on scientific subjects; (ii.) to examine Candidates, and to grant certificates of competency; and (iii.) to elevate the profession of Consulting and Analytical Chemistry by setting up a high standard of scientific and practical proficiency and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the

Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University approved by the Council, or in the laboratory of a Fellow of the Institute, with the object of adopting the profession of Analytical and Consulting Chemistry. *The Intermediate Examination*.—Candidates for admission to the Intermediate Examination are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Advanced Mathematics; (ii.) Mechanics and Chemical Engineering; (iii.) Metallurgy; (iv.) Geology and Mineralogy; (v.) Physiology; (vi.) Bacteriology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' training in a recognised Institution as indicated above, and work systematically for two other years in the laboratory of a Fellow of the Institute. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also passed in at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. *The Final Examination for the Associateship (A.I.C.)*.—Any Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *Fellowship (F.I.C.)*.—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of Applied Chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (Price One Shilling) of Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C.

IMPERIAL COLLEGE OF CHEMISTRY AND PHARMACY, 49 and 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction is given at this College in Pharmacology and Therapeutics, *re* the Institute of Chemistry Examination. Students attending the College visit technical works.

THE POLYTECHNIC, 309, Regent Street, W.—University of London Preparation Classes. Chemistry: R. A. Ward, F. E. Weston, B.Sc., F. Harvey, W. H. Collier, and H. R. Ellis, B.Sc.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Mr. Robert H. Pickard, D.Sc.(Lond.), &c., assisted by Messrs. Jos. Yates, W. O. Littlebury, A.I.C., and Jos. Kenyon. Session opens Monday, Sept. 10. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 2½d.).

REDRUTH SCHOOL OF MINES, CORNWALL.—Principal, Howard C. Ridding, A.R.S.M., F.I.C., assisted by a staff of Mining Engineers and Mine Surveyors. Courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Shorter Courses are also held in the above-named and cognate subjects to meet the requirements

of those having a limited time at their disposal and Prospectors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application to the Registrar. Session commences Wednesday, Sept. 12.

COUNTY TECHNICAL LABORATORIES, Chelmsford.—The new buildings are now open, and comprise facilities for practical instruction in Chemistry and Biology in their relation to Agriculture. Lecturer in Agricultural Chemistry: G. Clarke, F.I.C., assisted by H. Neville, B.Sc., A.I.C., V. H. Kirkham, B.Sc., A.I.C., and others. Prospectus free on application.

LEEDS INSTITUTE: TECHNICAL SCHOOL, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in over sixty subjects of Science and Technology, among which are:—Chemistry (Inorganic and Organic), Chemical Calculations and Principles of Analysis, by Mr. R. E. Barnett, B.Sc., A.R.C.S., Mr. J. B. Murray, Mr. A. McFarlane, and Mr. F. R. Penn; Metallurgy (Theoretical and Practical) and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Gas Manufacture, by Mr. W. E. Pettigrew; Oils and Fats, by M. W. Dillon; Magnetism and Electricity, Practical Physics, &c., by Mr. J. E. Tindall, B.A., B.Sc.; Botany, Lectures and Practical Work, by Mr. N. Walker; Photography, by Mr. S. E. Bottomley. Fees: from 7s. 6d. per session. Group courses arranged for Students engaged in Chemical Industries. Session commences Sept. 17th. Prospectuses of various Classes free on application to the Head Master.

CITY OF LEEDS HIGHER EDUCATION DEPARTMENT.—Courses of Evening Classes have been arranged for the Minor Examination of the Pharmaceutical Society, in which the whole Syllabus will be covered in three Winter Sessions. Chemistry: Mr. S. Parrish, B.Sc., A.R.C.S., Chief Lecturer in Chemistry, Central High School. Botany: Mr. Norman Walker, Assistant Lecturer in Botany, Leeds University. Pharmaceutics: Mr. J. H. Gough, Ph.C., F.C.S., Demonstrator in Materia Medica and Pharmacy, Leeds University. Full particulars from Mr. James Graham, Secretary for Higher Education, Education Offices, Leeds.

THE MUNICIPAL SCHOOL OF TECHNOLOGY, Sackville Street, Manchester.—This fine building occupies an area of upwards of 6800 square yards, and is six floors in height. Its equipment, which is nearly complete, is on a scale of great magnitude. It comprises laboratories and workshops for Mechanical, Electrical, Sanitary and Hydraulic Engineering, for the Textile industries, for Photography, Collotype and Photo mechanical processes, for the Letterpress and Lithographic industries, and for the industries included within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises, in addition to ample accommodation for pure Chemistry, laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity. The School is now established as the Faculty of Technology in the University of Manchester, and students of the School fulfilling the conditions can now proceed to the Degrees of Bachelor and Master of Technical Science (B.Sc. and M.Sc. Tech.).

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THE CHEMICAL NEWS.

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ON RADIO-ACTIVITY AND RADIUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

THE speaker commenced by saying that so little was known about this subject that it was the duty of every worker to throw his knowledge into the common pot, to be boiled down and assimilated into something useful. He asked what was the origin of the heat given out by radium, and, supplying the answer himself, said it must be due mainly to the sudden arrest of the discharged α -particles. He pictured to himself an atom of radium as a stellar system of electrons and groups of electrons revolving round each other with velocities of the order of that of light; those on the extreme outer surface of the system being more loosely held are liable to be thrown off tangentially, when they travel in straight lines, with scarcely diminished speed. The β -particles, or electrons, are so small that they penetrate solid bodies to a considerable depth, but the α -particles are large, and in spite of their enormous velocity cannot penetrate more than a few centimetres of air, and are stopped by a thin aluminium screen. It is evident that the sudden arrest of the atoms moving with such velocity would evolve heat. Indeed, in the spinthariscopes we see the effect in the splash of light; and in other circumstances the surrounding medium becomes warm. He had an idea—it had scarcely got as far as a hypothesis yet—that a molecule of radium locked up in a rock mass and compressed in the interior of the earth would not throw off particles, but would remain in a state of suspended animation. He had tried experiments with pitchblende, and the results showed that $\frac{1}{4}$ inch of the powdered mineral, compressed in a short lead tube, had exactly the same action on a photographic plate as 2 inches of the same powder in a longer tube. This is an additional argument in favour of the action being one of surface only.

The speaker concluded by describing an experiment in which $23\frac{1}{2}$ m.grms. of radium bromide, enclosed tightly in a brass box and embedded in ice, failed to show any melting effect in forty-eight hours.

RADIO-ACTIVITY.†

AT a meeting of the two divisions of Section A, on August 6th, a discussion took place on "Radio-activity and the Internal Structure of the Earth." It was opened by the Hon. R. J. Strutt, and a discussion ensued, in which Professor Milne, Professor Gregory, Sir William Crookes, Sir George Darwin, Sir W. Ramsay, Mr. Oldham, Professor Lamb, and Mr. Soddy took part, Mr. Strutt briefly replying to the whole. The discussion has attracted much interest, and many letters from leading men of science have appeared subsequently in *The Times* on the subject of radium. In view of the importance of the theoretical problems thus advanced, a reprint of all the important letters which have appeared will be of present and future interest. We preface them by an abstract of the proceedings at the British Association (Section A) meeting, as far as they bear on the physical and chemical problems centred in radium.

The Hon. R. J. STRUTT said that it had long been supposed that the internal heat of the earth was merely a remnant of the heat generated by contraction of a primeval nebula. This theory appeared until lately the only possible one; it was open, however, to the objection that in that

case the time which could have elapsed since the earth was red-hot became very short—much shorter, in fact, than the requirements of geology could easily admit. Some kind of "modus vivendi" had been reached between geologists and physicists on this matter. It may be doubted, however, whether the result of the controversy was really satisfactory to either party. Two years ago the suggestion was made by several writers that there might be enough radium in the earth to account for the internal heat. Rutherford calculated from some data given by Elster and Geitel that if the earth contained throughout its volume as much radium as a sample of clay examined by them, the temperature gradient at the surface would be about accounted for. I have recently examined a large number of rocks, both igneous and sedimentary, and have been led to the conclusion that there is very much more radium in all of them than would be needed to maintain the earth's internal heat if the earth were constituted of rock throughout. From this I conclude that the interior of the globe does not contain radium, and that in all probability its composition is quite different in other respects also from that of surface materials. My data for the quantity of radium in rock point to a thickness of at most forty-five miles for the earth's rocky crust. Such a thickness of rock would contain amply sufficient radium to maintain the earth's temperature gradient. Calculation on these premises, on the assumption that the thermal conductivity of rock is not much affected by change of temperature, proves that the internal temperature at the bottom of the crust (forty-five miles down) would be about 1500°C . The inside nucleus, heated by the crust of radium-containing material, must be at this uniform temperature throughout, just as a loaf of bread, which has been in an oven long enough, takes up a steady temperature equal to that of the walls of the oven. I have found in discussing the subject with scientific friends who are not concerned with the detailed development of radio-activity that one objection is specially felt. It is urged that a gramme of radium diffused through an enormous volume of rock may not develop nearly so much heat as it would do if concentrated. In answer to this it may be replied that—(1) there is no reasonable doubt that the heat development of radium is intimately associated with its peculiar electrical behaviour. Indeed, according to Rutherford's data, it can be quantitatively accounted for as the kinetic energy of the α -particles emitted. The rate of emission of α -particles by pitchblende, as measured by ionisation, is exactly what might be expected on the view that the radium atoms contained in the mineral are as energetic as they would be if they were all collected together. (2) Direct measurements made by Pegram on uranium and thorium have shown that these feebly active elements give about the amount of heat which their activity would lead one to expect. I think that these considerations leave no reasonable ground for the objection above mentioned.

Sir WILLIAM CROOKES made some remarks, which are reproduced in full in preceding column.

Sir W. RAMSAY referred to an experiment which pointed to a different conclusion from that drawn by Sir William Crookes. He had inserted in the hollow bulb of a thermometer an extremely small portion of the emanation of radium, and the readings of the thermometer so treated could be compared with those of another thermometer which had no radium. The readings of the treated thermometer remained for three weeks some three-quarters of a degree higher than those of the other.

RADIUM.

THE following letters have appeared in *The Times* :—

(August 9, 1906).

SIR,—In your yesterday's issue, under heading "British Association," I read, "In the Mathematical and Physical Section, a discussion was opened by Professor Soddy on

* Remarks made during the discussion on "Radio-activity and the Internal Structure of the Earth," at the meeting of the British Association, Section A, August 6th. (See "Radio-activity," above).

† British Association, York Meeting, 1906.

the possible transmutation of the elements. . . . The statement that the production of helium from radium has established the fact of the gradual evolution of one element into others was not seriously questioned."

I wish to remark that an isolated experimental discovery by Sir William Ramsay and Professor Soddy, brilliantly interesting as it is, and solidly instructive as it is towards the theory of radium, suggests nothing more towards any modification of the atomic doctrine proposed some 2500 years ago by Democritus and universally adopted by chemists and other philosophers in the Nineteenth Century, than does Ramsay's original discovery of helium as an emanation from the mineral cleveite. The obvious conclusion from the two discoveries is that cleveite and radium both contain helium.

I cannot refer, thus publicly, to discussions on radium in the meeting of the British Association which commenced last Wednesday in York without protesting against the hypothesis that the heat of the sun or earth, or other bodies in the universe is due to radium. I believe it is mainly due to gravitation; and I believe that the experimental results on which the radium hypothesis has been built give no foundation on which it can rest.—I remain yours faithfully,

KELVIN.

Aix les Bains, Aug. 5.

(August 10, 1906).

SIR,—I venture to think that the thanks of the public are due to Lord Kelvin for his timely and outspoken protest against the conclusion being drawn, from the evidence at present before us, that it is proved that there is a "gradual evolution of one element into others." No one has yet handled "radium" in such quantity or in such manner that we can say what it is precisely. That helium can be obtained from "radium" appears to be proved; but no proof has yet been given that it is not merely contained in it. As I remarked at York last week, physicists are strangely innocent workers; formulæ and fashion appear to exercise an all-potent influence over them.

There was a time when the expression "scientific caution" meant the highest degree of caution, and it was supposed to be the attribute of workers in science. Workers in the radium school appear to have cast caution to the winds, and to have substituted pure imagination for it. Among ourselves, we should always be at liberty to postulate the most crack-brained of hypotheses, to dream the wildest of dreams, as a means of guiding inquiry; but we should not court popularity on such a basis. By so doing we lose all claim to guide public opinion.—I am, Sirs, yours obediently,

HENRY E. ARMSTRONG.

(August 15, 1906).

SIR,—Lord Kelvin's letter in your issue of August 9 will, of course, receive respectful attention, and even in this holiday time the public may expect some reply. The fact that physicists have been unable to carry their veteran leader with them in some recent developments has been regretfully known—it is admitted, for instance, on the last page of the third edition of my "Romanes Lecture," as issued by the Clarendon Press—but it is also known that his brilliantly original mind has not always submitted patiently to the task of assimilating the work of others by the process of reading, and our hope has been that before long he would find time and inclination to look into the evidence more fully.

The evidence for the generation of helium may be briefly summarised thus:—Rutherford measured the magnetic deflexion of the α -rays, or positively charged particles shot off by radium emanation at a certain stage of its disintegration (for it does disintegrate, it is not permanent), and inferred that the mass of each particle was comparable with twice that of an atom of hydrogen; consequently that

the projected particles were material, and that the projected matter, if it were any single known substance, must be either hydrogen or helium, and most likely helium. Ramsay and Soddy then enclosed some of the emanation in a vacuum tube, and examined its spectrum. There was no sign of helium at first—as there would have been had it been merely an ingredient in a mixture—but the helium spectrum gradually made its appearance, in the course of a day or two, at approximately the rate to be expected on the disintegration hypothesis. The loss of much activity by radium when its emanation is removed from it and the gradual return of radio-activity when time is allowed for fresh emanation to be formed, are also facts to be remembered. The rest of the evidence for the slow disintegration of atoms is of a less direct kind, but it is voluminous and varied, and seems to me extremely weighty.

Lord Kelvin's maintained opinion as to the heat of the earth and of the sun is of great interest. He and Helmholtz have both shown conclusively that if the sun is contracting at a certain slow rate—a yard or two per month, if I remember right, too small an amount to be detected as yet—gravitational energy is quite sufficient to account for the whole of its heat emission. The only question is whether or not the sun is actually shrinking at the prescribed rate. It is an efficient cause, and it may be the only cause in operation; or it may be supplemented by another, namely, by the conversion into ethereal radiation of some portion of the presumably vast store of intra-atomic energy, perhaps by a process so direct as partially to evade the intermediate stage of the random molecular motion called heat. For it is a suggestive question to ask why suns do not exceed a certain limit of size and temperature. Is it possible that under excessive conditions atomic disintegration begins to set in at more than the spontaneous rate?

As soon as solar shrinkage can be measured we shall know the proportion in which the two causes, the gravitational and the atomic, contribute to the total result.

As for the case of the earth: if the interior is hot at all—and about that there appears to be no doubt—heat must be flowing up through the crust: and this is the process utilised by Lord Kelvin in his calculation. It will be remembered that when he conceived the idea of applying this criterion to make a rough preliminary estimate of the lapse of time since the earth was molten, he expressly guarded his deduction by saying "provided no other process than conduction of heat occurs"; a proviso which clearly allowed for the now discovered generation of some heat *in situ* from a then unknown and quite unsuspected source.

I see a characteristic comment by Professor Armstrong in your issue of August 10. He and a few other chemists have before now shown themselves scornful of chemical results obtained by physical means; but they manage to absorb these results in the end. Chemists have an instinct of their own for arriving at such doctrines as the constitution of organic compounds and other admirable discoveries; and though occasionally it may happen that their methods of reasoning seem to us odd and unconvincing, they are ready, and even eager, to retort that ours are forced and unintelligible. But wisdom is justified of her children.—I am, Sirs, yours faithfully,

OLIVER LODGE.

The Hermitage, Bletchingley, Surrey.

(August 15, 1906).

SIR,—As Lord Kelvin in his letter of August 9 referred unfavourably to the views which I expressed in opening a discussion in Section A of the British Association at York on the internal heat of the earth, I hope it may not be improper for me to draw attention to the other side of those questions which he raises. First, as to the production of helium from radium. Lord Kelvin seems to consider that the experimental results on this subject prove nothing more than that helium is an original constituent of radium. This view does explain the fundamental fact, independently

vouched for by Ramsay and Soddy, by Himstedt and Meyer, and by Curie, that the supply of helium obtainable from radium is constantly renewed. If all helium is removed from a sample of radium it is found that after an interval a further supply can be extracted. This can only mean that helium has been generated since the last extraction.

Lord Kelvin does not enter into any detailed criticism of the view that the internal heat of the earth is due to radium. He merely describes it as a hypothesis. I cannot think this description a fair one. I have attempted to show by quantitative experiment that the amount of radium in the earth's crust is so large that we are compelled to suppose that crust very thin in order to explain why the heat conducted out of the interior of the earth is not even greater than we find it to be by observation. I believe that Lord Kelvin does not refuse to accept my experimental results. Indeed, he has been so kind as to write to me very appreciatively of them. What, then, is his objection? It is true that gravitational condensation is a cause which must have once heated the earth. But we have no reason for supposing that any of the heat so generated still remains. If we did suppose so we should be face to face with the question, What becomes of the heat generated by the radium admitted to be present in the earth?

R. J. STRUTT.

40, Portman Square, W.

(To be continued).

SIZING PAPER WITH VISCOSE.*

By CLAYTON BEADLE.

In discussing this subject I feel compelled to say a few words in explanation of the subject chosen, namely, the use of viscose for paper sizing, which is still the subject of a patent. I feel that I must discuss the matter only in the light of the information which has already been made known, as I should not feel justified in going further than this. What I am about to describe and discuss is based on data already disclosed in connection with viscose.

I shall carefully omit all reference to the question of theory and deal as far as possible with that of fact, and confine myself to remarks on the manufacture and use of viscose in its application to paper.

The first stage of the manufacture of viscose is the preparation of what is called alkali-cellulose, or what was formerly known as Mercerised-cellulose, from the name of its inventor.

An alkali-cellulose adapted to the use of papermakers has approximately the following composition:—

Cellulose..	25 per cent.
Alkali ..	(NaOH) 15 per cent.
Water ..	60 per cent.

This is generally prepared by taking, say, 100 lbs. of well-beaten pulp containing 50 per cent moisture, and grinding the same in edge-runners. Whilst the grinding action is going on, a stream of caustic soda solution is added at 70° Tw. and equal in weight to the weight of the wet pulp taken. The alkali should be added in a slow stream; if added too quickly the stuff gets greasy and the stones are liable to skid, but if added slowly the alkali is taken up by the cellulose; the whole operation takes about three-quarters of an hour. The so-called alkali-cellulose consists of fibres swollen by absorption of alkali and water, and when cotton or linen pulp is used is not unlike snow in appearance. This alkali-cellulose should be stored in a cool place, the temperature not exceeding 60° F., in air-tight tubs kept from contact with the air. If the air is allowed to get in contact with the alkali-cellulose the carbonic acid of the air combines with the alkali, producing carbonate of soda and rendering the cellulose no longer susceptible to attack of carbon bisulphide. I made

it a regular practice to examine different batches of alkali cellulose, the results of which were recorded. With care, great regularity can be ensured. A simple method of examination is to weigh out 10 grms. of alkali-cellulose, taking care that an average sample is selected. This is added to about 150 c.c. hot water, agitated for a few minutes, and filtered through muslin into a litre flask, and washed with hot water until free from alkali. The filtrate is cooled, made up to 1000 c.c. An aliquot portion is titrated after further dilution with recently boiled and rapidly cooled distilled water in presence of phenolphthalein until red colour is just discharged, then to neutral tint with methyl-orange. The residue on the filter is dried at 105° C. Weight + 7 per cent, equals air-dry weight of cotton or linen cellulose, or if from wood pulp one-ninth is added for air-dryness.

On account of the liability of alkali-cellulose to be affected by heat it has to be stored in the cool; the effect of heat is to bring about a molecular change in the alkali-cellulose, rendering it of less service in the sizing of paper, as will be demonstrated hereafter. For all ordinary purposes alkali-cellulose can be stored for several weeks or even months in the temperature above given, but if brought into a temperature such as prevails in the summer months it would last only a few days.

The word "crumbs" is used in England to designate alkali-cellulose, in consequence of the close resemblance of alkali-cellulose as prepared for papermaking to ordinary bread crumbs.

The alkali-cellulose has next to be put into a revolving barrel or churn, which is about three-fourths filled, and carbon bisulphide equal to one-tenth the weight of the alkali-cellulose is then added, and the churn revolved for fifteen minutes to thoroughly mix the ingredients; it is then allowed to stand. It is best to do this at a uniform temperature, say at 70° F.; at this temperature the reaction takes about two hours. The carbon bisulphide combines with the alkali-cellulose to form a compound which is soluble in water, the colour changes from white to brilliant yellow, and darkens to a brown shade if allowed to remain long before dissolving. In mass reactions even in 1 cwt. batches one has to guard against sudden rise of temperature. Little or no rise is noticed when the initial temperature is in the neighbourhood of 60° F., but at 75° to 80° the temperature may rise, due to the rapidity of the reaction, to such a final temperature as to bring about a complete reversion of viscose, producing again insoluble cellulose as a large ball or lump in centre where the temperature has reached its highest point.

The yellow mass, which has somewhat the consistency and appearance of fine particles of butter, is discharged from drum and agitated with one and a-half times its weight of water, giving rise to a yellow thick viscous solution to which the name of "Viscose" has been given. This solution contains 10 per cent of cellulose. In course of time the solution darkens in colour, changing from that of golden syrup to ordinary molasses.

I should like to point out the importance of making the viscose under the most favourable conditions, as so much depends upon this as to whether the result is good or not. This remark applies, of course, to all applications of viscose, each application requiring viscose manufactured in a particular manner. First of all I would point out that the time the alkali-cellulose is kept before the carbon bisulphide treatment, alters the viscosity of the solution; thus, if it is kept a long time, the viscosity of the solution produced from the same is lowered; if, on the other hand, the solution is made up from fresh crumbs, it has its maximum viscosity; but alkali-cellulose can be stored for weeks in a refrigerator without bringing about very much change in the viscosity of the solution produced from the same. The molecular change can, therefore, be promoted by heat or arrested by refrigeration; the exact change or rate of change being dependent upon the temperature. At a higher or critical temperature the change is so rapid as to break down the cellulose to a useless product in a few

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minutes. At the freezing point (or below) the change is practically arrested. One could draw up a curve to illustrate the rate of change at different temperatures which would be highly instructive to those engaged in viscose making.

It follows then that if alkali-cellulose is stored in a hot place the resulting solution is comparatively thin; even if the alkali-cellulose is kept for only a couple of days in a warm room the solution would be very much thinner and less viscous. It is possible, by altering the temperature, to very much control the condition of the solution to suit various requirements. It cannot be said, however, that time and temperature are altogether interchangeable factors, as there are conditions of solution brought about by storing at moderate temperatures which cannot exactly be imitated by elevating the temperature for a short period. The slow process of ageing is almost always preferable.

Then, again, the amount of alkali in comparison with that of cellulose present, very much influences the viscosity of the resulting solution; within limits, the higher the alkali the lower the viscosity, and *vice versa*. The alkali can be lowered to say 12 per cent on the weight of alkali-cellulose or 50 per cent on cellulose, but for most ordinary purposes it is not advisable to do this, because there is a danger of leaving a considerable proportion of the fibres still unacted upon. There is, therefore, no economy in sparing the amount of alkali if such results in certain of the fibres being left unacted upon. The composition given above is about the most useful all-round one. The viscosity of the solution can be lowered by the addition of caustic soda direct to the viscose solution. This, however, is not to be recommended for paper sizing.

The effect produced by the viscose in strengthening and hardening the paper is more dependent upon viscosity of the solution than upon its percentage strength in cellulose. This is a cardinal point to be remembered. The higher the viscosity the greater the strength-giving effect. If, given two solutions of equal strength (say 10 per cent), one prepared to be very viscous, and the other very thin or non-viscous, it is quite possible that the former may have five times the strength-giving effect of the latter. It would be necessary, therefore, to use five of the latter to one of the former. The art, therefore, of preparing viscose for this purpose is to do so in such a way as to give its maximum strength-giving and hardening effect, so that the desired result may be brought about by the use of the minimum quantity of viscose. It is, however, necessary to distinguish between a "ropiness" due to untreated or partially treated cellulose and the proper viscosity of the solution.

Viscose has a property of coagulating or becoming insoluble. The solution in time hardens to a jelly, forming again insoluble cellulose, but in a hydrated condition. If, however, the solution is extremely dilute, as it is in an ordinary paper-makers' beater, and agitation is going on at the same time as coagulating is taking place, instead of homogeneous jelly being formed, a flocculent precipitate of cellulose is produced, which, in contact with the pulp on the paper machine can be made to agglomerate into one continuous mass, and give strength to the paper by glueing the fibres together. The art of viscose sizing is to bring this change about so as to give the maximum benefit to the paper. It is advisable to use the viscose solution within a short period of the time of manufacture; it will not keep indefinitely, and for this reason it should be by preference made in the paper mill where it is to be used. The effect produced is not unlike that due to prolonged beating with dull tackle, whereby some of the fibre is munched up into a gelatinous mass of hydrate, which has the power of acting as an adhesive, and glues the fibres together when made into pulp.

When a dilute solution of viscose is added to the paper-maker's beater precipitation does not take place quickly, particularly with freshly made viscose. It is necessary, therefore, to add some substance which will bring about the precipitation of the cellulose, but in such a manner as to preserve its flocculent sticky condition. Ordinary

mineral acids will precipitate it at once, but destroy its good qualities; alum, also, is too acid a substance, and in a measure has the same effect as mineral acids. Something is needed to precipitate the cellulose in a more gentle fashion; this can be accomplished by the addition of magnesium sulphate or zinc sulphate. These salts decompose the soluble compound, leaving the cellulose suspended in contact with the fibres and the pulp neutral.

In order to appreciate the influence of various slight modifications in the *modus operandi* of working I will give a few details of one or two trials which I have conducted. I would point out that I have conducted somewhere about two hundred viscose paper-sizing trials, some purely laboratory investigations and others done on a large scale; in nearly all cases the quantities, details, temperature, time, &c., were carefully noted, and I feel, therefore, in regard to any conclusions that I may have arrived at, that I speak with a certain amount of authority as having had a fairly extensive experience.

No. 15. 10% P.W.L. Crumbs. (Composition as above stated).

February 13, 1897.

Made up into viscose as follows:—

5% solution made by adding 50 parts water to 50 parts of 10% solution.

6½% solution is made by adding 26 parts water to 50 parts of 10% solution.

8% solution is made by adding 12½ parts water to 50 parts of 10% solution.

Paper Trial No. 16. February 16, 1897.
(Beaten February 4, 1897).

800 parts 5% mechanical aspen.

7200 " of water.

10 " 5% P.W.L. viscose.

In 10 minutes 12 parts 5% zinc sulphate.

In 5 " 8 " 5% resin solution.

In 5 " 3 " 5% potash alum.

In 5 " made into paper.

Paper Trial No. 17. February 16, 1897.
(Beaten February 4, 1897).

800 parts 5% mechanical aspen.

7200 " of water.

10 " 6½% P.L.W. viscose.

In 10 minutes 15 parts 5% zinc sulphate.

In 5 " 8 " 5% resin.

In 5 " 30 " 5% potash alum.

In 5 " made into paper.

Paper Trial No. 18. February 16, 1897.
(Beaten February 4, 1897).

800 parts 5% mechanical wood (aspen).

7200 " of water.

10 " 8% P.L.W. viscose.

In 10 minutes 15 parts of 5% zinc sulphate.

In 5 " 8 " 5% resin.

In 5 " 30 " 5% potash alum.

In 5 " made into paper.

Paper Trial No. 19. February 17, 1897.
(Beaten February 4, 1897).

500 parts 5% mechanical aspen.

7200 " of water.

10 " of 10% P.L.W. viscose.

In 15 minutes 16 parts of 5% zinc sulphate.

In 5 " 8 " 5% resin.

In 5 " 3 " 5% potash alum.

In 10 " made into paper.

Paper Trial, No. 20.

As above, but containing no viscose, &c.

Below are the strength tests done upon Samples 16—20, selecting samples of 5/1000 inches in thickness; the strength is expressed in lbs. per strip of 1 inch width :—

No.	16.	17.	18.	19.	20.
	5'9	5'7	4'4	5'2	2'9
	4'2	6'2	4'0	4'9	2'8
	4'1	5'8	4'4	5'2	3'2
	4'3	3'5	4'0	4'9	2'7
	5'4	3'5	4'0	4'7	3'0
	6'0	3'8	4'2	4'7	2'5
	2'8	4'5	4'3	5'3	2'0
	5'4	4'5	4'4	4'4	1'9
	3'4	4'8			3'7
	4'2	3'7			2'0
					2'3
					2'0

No. of tests	10	10	8	8	12
Mean strength ..	4'57	4'60	4'22	4'91	2'60
Reducing No. 20 to 100 for comparison	175	177	162	188	100

The last line shows the gain in strength due to the added viscose, when 100 is deducted from each.

Paper Trial No. 28. February 24, 1897.

800 parts of 5% mechanical aspen beaten Feb. 4, 1897.
7200 " water.

Made into paper.

Summary of strength test .. $\frac{39'2}{2'02} = 19'04$.

Paper Trial No. 29. February 24, 1897.

800 parts of 5% mechanical aspen beaten Feb. 4, 1897.
7200 " water.
8 " 5% resin.
3 " 5% potash alum.

Made into paper.

Summary of strength test .. $\frac{44'5}{2'13} = 20'9$

Paper Trial No. 30. February 24, 1907.

800 parts of 5% mechanical aspen beaten Feb. 4, 1897.
7200 " water.
5 " 8% P.L.W. viscose.

(Average of five mixings alkali cellulose about 10 days old and stored out of doors). Viscose about 12 hours old.

In 15 minutes 12 parts of 5% zinc sulphate.
In 5 " 8 " 5% resin.
In 5 " 30 " 5% potash alum.
In 5 " made into paper.

Sample of the above viscose gave 8'90% of bone-dry cellulose.

Summary of strength test .. $\frac{65'7}{2'14} = 30'7$

No. 29 : No. 30 :: 100 : 148

No. 28 : No. 30 :: 100 : 153

Paper Trial No. 31. February 25, 1897.

800 parts of 5% mechanical aspen beaten 1 hour before.
7200 " water.

Summary of strength test .. $\frac{65'0}{1'92} = 33'8$

Paper Trial No. 32. February 25, 1897.

800 parts of 5% mech. aspen beaten about 1½ hrs. before.
7200 " water.
8 " 5% resin.
3 " potash alum.

Summary of strength test .. $\frac{67'1}{1'85} = 36'2$

Paper Trial No. 33. February 25, 1897.

800 parts of 5% mech. aspen beaten about 2½ hrs. before.
7200 " water.
5 " 8% P.L.W. crumbs about 12 days old.
Viscose average three mixings about 12 hours old.
Made February 24, 1897.

Sample of the above viscose gave 8'32% of bone-dry cellulose.

Summary of strength test .. $\frac{70'9}{1'67} = 42'4$

No. 31 : No. 33 :: 100 : 125

No. 32 : No. 33 :: 100 : 117

Paper Trial No. 34. February 26, 1897.

800 parts of 5% mechanical aspen beaten Feb. 25, 1897.
7200 " water.

Summary of strength test .. $\frac{64'7}{2'15} = 30'1$.

Paper Trial No. 35. February 26, 1897.

800 parts of 5% mechanical aspen beaten Feb. 25, 1897.
7200 " water.
8 " 5% resin.
30 " 5% potash alum.

Summary of strength test .. $\frac{74'8}{2'17} = 34'4$.

Paper Trial No. 36. February 26, 1897.

800 parts of 5% mechanical aspen.
7200 " water.
5 " 8% viscose.

Made from P.L.W. crumbs about 14 days old. Made into viscose Feb. 25, 1897. Average of three raisings.

In 15 minutes 20 parts of 5% zinc sulphate.
In 5 " 8 " 5% resin.
In 5 " 3 " 5% potash alum.

Sample of the above viscose gave 8'12% of cellulose.

Summary of strength test .. $\frac{112'1}{2'4} = 46'7$

Comparison of strength tests of Nos. 34—36 :—

No. 34 : No. 35 :: 100 : 114
No. 35 : No. 36 :: 100 : 136
No. 34 : No. 36 :: 100 : 155

Added Cellulose.

In viscose-engine sizing, taking experiments Nos 16—20, also Nos. 34—37 :—

Viscose equal to added cellulose on paper.	Total added strength.	Equal to added strength for each 1% of added cellulose.
1'00%	54%	54%
1'25	75	59
1'62	77	47
2'50	88	35

Tables 15 to 30 give details of various viscose trials; No. 15 shows the way the different strengths of viscose solution were made up for the purposes of trials. The object of these trials was to determine the strength giving effect of viscose on very weak material, such as ordinary newspaper, which is composed for the most part of mechanical wood; it will be noticed that rosin size is used in most cases equal to 1 per cent on the weight of the paper.

Trial No. 20 was made without the addition of rosin or viscose for the purposes of comparison. In each case the first chemical ingredient was added ten or fifteen minutes after the viscose, then five minutes elapsed before the addition of rosin, and another five minutes before the addition of alum, and in most cases five minutes after this the pulp was made up into paper. The strength tests were done as follows :—

Five to ten strips of 1 inch wide by 4 inches long were cut and tested on a "Marshall" tester; each test was noted, as also the thickness of pieces, in order that corrections should be made in the strength test for any variation in the thickness of the sheet.

The strength tests of Nos. 16 to 20 are given in detail. The figures at the bottom show the relative strengths of the various mixtures when the waterleaf No. 20 is reduced to 100, showing the great gain on the addition of viscose.

Passing to trials Nos. 34 to 36, No. 34 is waterleaf alone, No. 35 is the same with the addition of 1 per cent of rosin and the necessary alum, No. 36 is the same but with the addition of viscose, the details of the manufacture of which are given, and the necessary amount of zinc sulphate required for the precipitation. Above are given the relative strengths of the foregoing trials when the waterleaf is reduced to 100. It should be noticed that the one containing 1 per cent of rosin is 14 per cent stronger than the waterleaf. This is in contradiction, I believe, to statements made by Hertzberg and Hofmann to the effect that rosin decreases the strength of paper.

In a recent lecture delivered in London I gave the result of all the determinations I had made for strength of paper with and without rosin. My conclusion was, and of this I have no doubt, that very weak papers, such as those composed almost entirely of mechanical wood, are increased in strength by the addition of rosin, whereas papers consisting of very strong fibres decrease. Papers such as those given in the trials herein described are all increased in strength by the addition of rosin.

It will be noticed from Trial No. 36 that the addition of viscose has added to the strength of the paper in question to the extent of 36 per cent over and above the strength of the rosin sized paper containing no viscose, and 55 per cent over and above the waterleaf paper.

Turning briefly to the Trials Nos. 28 to 30, it will be noticed that No. 29 (containing no viscose) is much weaker than No. 30 (with viscose); the addition of viscose, as in this case, added to the strength of the paper to the extent of 48 per cent, or showing a total increase of strength above waterleaf of 53 per cent. Turning back to the summary embodying the results of Nos. 16 to 20 and 34 to 36, it will be noticed that the papers in question show an average increase in strength of 54 per cent for the addition of 1 per cent of cellulose as viscose. When 1.25 per cent is added the total increase in strength is 75 per cent, making an increase in strength on the waterleaf of 59 per cent for each 1 per cent, of added viscose. When we come to the addition of 1.62 per cent of cellulose as viscose, the total increase is 77 per cent, showing a very slight addition on the 1.25 per cent, and, consequently, a very much lower figure for each 1 per cent of added viscose (*viz.*, 47 per cent). When 2.5 per cent cellulose as viscose is added, being double the 1.25 per cent, the strength is only increased from 75 per cent to 85 per cent, and the increase in strength for each 1 per cent of added viscose drops down to 35 per cent.

The various trials that I have made have led me to the conclusion that there is a great distinction between the percentage rate of increase of strength of the paper and the absolute increase in strength of the paper where one is dealing with the question of added cellulose or gelatin.

It is possible from the trials cited, which were conducted in a manner to observe any slight difference that might arise, to arrive at certain definite conclusions:—

First of all, the maximum strength for 1 per cent of added cellulose in the form of viscose is imparted to the paper when viscose of the maximum viscosity is used. The maximum effect for each 1 per cent of cellulose is obtained when small amounts are added (*i.e.*, 1 per cent or less); thus 2 per cent would not exert double the effect upon the paper that 1 per cent does, nor would 4 per cent exert double the effect upon the paper that 2 per cent does.

There appears, furthermore, to be a limit to any increase of strength due to the addition of viscose; for example, a point may be reached in one paper on the addition of

5 per cent of cellulose, and in another on the addition of 10 per cent, beyond which the additions of further quantities of cellulose as viscose would give no increase of strength.

I would point out, in conclusion, that the effect of viscose sizing is somewhat similar to the effect of excessive or prolonged beating in the Hollanders. In the case of prolonged beating the fibres are more or less hydrated, and a certain amount of cellulose is formed which causes the stuff to work wet, and gives to it greater strength and hardness. In the case of viscose sizing, instead of affecting the fibres themselves, the cellulose hydrate is added or precipitated, giving to the pulp somewhat the same properties as if the beating had been prolonged.

A proper appreciation of the factors which go to produce viscose of suitable properties for paper sizing is indispensable. It is no difficult matter to produce viscose that will be useless for the purpose. On the other hand, with a careful study of the conditions and proper control in the factory the best results can be got with much smaller quantities than is commonly supposed. This applies with equal force to sizing of webbing, of which I have had considerable experience. I do not wish it to be supposed that this article would give sufficient information to enable manufacturers to size with viscose. It will, however, I hope, put them on the right path and indicate to them the direction along which they must work to produce satisfactory results.

THE DETERMINATION OF THE COMPOSITION OF NITROGEN IODIDE.

A SHORT STUDY IN CHEMICAL HISTORY.

By F. D. CHATTAWAY.

It is always interesting to follow the steps by which a definite conception of the composition and structure of a familiar compound has been gained. Sometimes we owe practically all our knowledge of a substance to its discoverer, but it more often happens that many minds and hands have added here a fact and there a theory until our present view of its nature and constitution has been built up.

It is seldom possible to allot to each investigator his precise share in the result, since it frequently happens that work on a different and apparently unrelated part of the subject throws unexpected light on the problem under consideration.

An interesting fragment of the history of chemistry is that which deals with the development of our present views of the nature of the so-called nitrogen iodide. Every schoolboy knows how easily this black explosive solid can be produced by mixing solutions of iodine and of ammonia.

It was first prepared by Bernard Courtois nearly a century ago, and a description of the curious new substance was included in a paper, read before the Institute on November 29th, 1813, in which he announced his discovery of the element iodine.

Courtois being too much occupied as a chemical manufacturer to continue the systematic investigation of the new element, this was undertaken by Gay-Lussac. In Gay-Lussac's laboratory and under his direction nitrogen iodide was first studied by Colin, who regarded it as a substitution derivative of ammonia of the composition NI_3 . Gay-Lussac himself in his great memoir on iodine explained its formation on the assumption that it has this formula. The compound about this time was also investigated by Vauquelin and Davy, who agreed with Gay-Lussac in regarding it as analogous to nitrogen chloride; that is, as ammonia in which all the hydrogen had been replaced by iodine. Mitscherlich later was led to assign to it the formula NI from the observation that both it and ammonium chloride were produced by the action of iodine trichloride on ammonia. Serullas, who after an interval

of some years studied it, expressed no opinion as to its constitution, but concerned himself mainly with its reactions, including the action of acids, alkalis, and water on a product which he prepared by mixing solutions of iodine monochloride and ammonia. So far the formula NI_3 was generally accepted.

The fact that hydrogen is a constituent of the compound was next established by the work of Millon, Bineau, and Marchand. For this purpose various methods were employed, including Marchand's dangerous experiment of heating the dry substance with lead chromate. These chemists brought forward the formulæ NHI_2 or NH_2I . Bineau came to the conclusion that the former must be correct, since in the product he analysed the nitrogen and iodine were present in the ratio of one atom of nitrogen to two atoms of iodine. He obtained this incorrect ratio by decomposing his material with hydrogen sulphide, and noting that approximately two molecules of hydrochloric acid were formed to one of ammonia.

The study of the compound was continued by Gladstone and Bunsen, who about the same time published accounts of their researches. Although they described new reactions of the substance and variations in the methods of preparing it, they chiefly concerned themselves with attempts to determine its elementary composition. Gladstone came to the conclusion that one compound only could be obtained, whose composition he represented by the formula NHI_2 . Bunsen, on the other hand, maintained that more than one distinct compound could be formed, and gave formulæ NH_3 , NI_3 and $\text{NH}_3 \cdot 4\text{NI}_3$ as the results of his two analyses. Gladstone, in a reply, pointed out that in the formation of nitrogen iodide by the interaction of iodine and ammonia, although nearly half the iodine appears as ammonium iodide, a trace of iodate is always found, a fact overlooked by Bunsen.

Schönbein, in a very interesting study of the action of the halogens on aqueous solutions of alkalis, also pointed out Bunsen's omission to observe the formation of iodate, and suggested that the reaction of iodine with ammonia was completely analogous to that of iodine with other alkalis, and that nitrogen iodide was formed by some decomposition of ammonium hypoiodite.

Many years later, Mallet analysed specimens of nitrogen iodide which, in purifying, he had subjected to the drastic treatment of long-continued washing with alcohol. From his results he concluded that a series of compounds existed, an inference which might be expected, inasmuch as the amount of decomposition depends on the conditions of such treatment.

The decomposition of nitrogen iodide by light, a most important fact in relation to its composition, was first noticed by Guyard, who proposed to use the substance for photometric purposes.

More recently, both Raschig and Szuhay discussed the work of previous chemists, but threw little fresh light on the subject. Lastly, Seliwanow has followed Schönbein, and sees in nitrogen iodide a derivative of hypoiodous acid. He attempted, but qualitatively only, to show that the formation of ammonium hypoiodite always preceded the precipitation of nitrogen iodide, and is one of the first products of the decomposition of the latter.

On reviewing all this work one is struck by the divergence in the analytical results of material obtained apparently by identical methods, as, for example, Gladstone and Bunsen's preparations of nitrogen iodide from saturated solutions of iodine and ammonia in absolute alcohol. It would appear either that different substances must have been obtained when the conditions were only slightly varied, or that the treatment to which the compound was subjected must have caused a partial decomposition which was not observed.

Moreover, not one of the chemists who studied the substance seems to have made a series of analyses to confirm the numbers on which his conclusions were based.

Further, the very frequent evolution of nitrogen in the various reactions described, although it generally escaped

notice, even when observed, was neglected in the explanation suggested.

When some eleven years ago the study of nitrogen iodide was undertaken by the present writer, it appeared to be universally accepted that a number of distinct compounds existed, although the belief was based entirely upon discordant analytical results which, upon close examination, were clearly untrustworthy. Not only did the numbers obtained by different observers agree in very few cases, but even those of the same observer often differed widely. Further, in no single case was any evidence brought forward to show that the material analysed was pure, and in no case were any data given to justify the assumptions made regarding the reactions on which the analyses were based.

The confusion of the whole subject at that time may still be seen in the statements made regarding nitrogen iodide in some of the better known dictionaries and text-books.

Since that date, however, the composition of nitrogen iodide has been established beyond doubt, a fair amount of evidence has been brought forward in support of a constitutional formula, and its chief reactions and decompositions have been simply and quantitatively explained, while, further, the varied analytical results of previous workers have been shown to be due either to the partial decomposition of the compound by washing, leading to loss of ammonia, or to the loss of nitrogen caused by light, or to its partial decomposition by alcohol.

The first step in the elucidation of the tangle was a careful qualitative study of the conditions necessary for the preparation of pure nitrogen iodide and of those which obviously brought about its decomposition.

It was found especially that washing it with water, if this was at all prolonged, caused a liberation of iodine, that alcohol also very readily reacted with it, while even the diffused light of a laboratory falling upon it set free immediately both nitrogen and iodine. Obviously, therefore, light must be excluded in the purification and analysis of the compound, the use of alcohol in its preparation and purification should be avoided, and washing by water must only be carried to a point sufficient to remove free adhering ammonia.

A method of analysis had next to be sought which, while exact, could be expeditiously carried out and so admit of a very large number of analyses of specimens prepared by all known methods.

Such a simple and rapid process was found in the decomposition of the compound by sodium sulphite. When a solution of this substance reacts with nitrogen iodide suspended in water, a colourless acid solution is obtained containing only sodium sulphate, ammonium iodide, and free hydriodic acid, disregarding, of course, the distribution of the bases among the acids. This reaction, one of the very few where nitrogen iodide decomposes in one way only, was thoroughly investigated, and upon it a method of analysis was based.

Numbers of experiments showed that if light was excluded no nitrogen was disengaged in the free state, but that all of this element contained in the compound was obtained as ammonia, and that this result was not affected by the sulphite being added rapidly in excess or slowly drop by drop, or by the consequent non-appearance or appearance of free iodine in the liquid.

All the products formed in this reaction were estimated in a variety of independent ways, and the quantity of sulphite oxidised was found to be exactly double the amount equivalent to the hydriodic acid produced; that is, Na_2SO_3 produced HI .

This fact having been established, a simple method of analysis fulfilling all the conditions previously laid down was available. The solution resulting from the action of normal sodium sulphite upon nitrogen iodide is always found to be acid, since the amount of hydriodic acid produced is greater than that required to neutralise the ammonia simultaneously formed. This excess of acid can easily be estimated by standard alkali, and since sodium

sulphate is neutral and the total amount of hydriodic acid formed is accurately known from the quantity of sulphite used, the difference between the amount of hydriodic acid produced and the amount present as free acid represents the amount neutralised by the ammonia of which it is consequently a measure.

The actual analysis was carried out as follows:—A small quantity of nitrogen iodide was rapidly washed a few times on a filter-pump and suspended in water in a flask, light being excluded. A decinormal solution of sodium sulphite was then added slowly, drop by drop, until the iodine liberated towards the end of the reaction had disappeared, a little starch paste being used as indicator. Litmus was then added, and the free acid estimated by a decinormal solution of ammonia. The accuracy of these extremely simple titrations having been thoroughly established, a large number of analyses were made of specimens of nitrogen iodide prepared in every way known to yield it. It was found that the relation between the ammonia and hydriodic acid was absolutely invariable, two molecules of ammonia were always produced to three molecules of hydriodic acid. However nitrogen iodide is prepared, and whatever its condition, dry or moist, crystalline or amorphous, compact or finely divided, the relation between the ammonia and hydriodic acid is the same. In this way it was proved that in all reactions which are known to yield nitrogen iodide only one individual compound is formed, and that in its molecule two atoms of nitrogen are associated with three atoms of iodine.

It was further found that when nitrogen iodide decomposes under the influence of light it breaks up quantitatively into nitrogen and hydriodic acid. Consequently, its molecule must contain the same number of atoms of hydrogen as it does atoms of iodine. Since, therefore, in its molecule two atoms of nitrogen are associated with three atoms of iodine, and these again with three atoms of hydrogen, the simplest possible formula for nitrogen iodide is $N_2H_3I_3$.

That this formula correctly represents the composition of nitrogen iodide was further proved by a large number of analyses of weighed amounts of the pure dry substance prepared in different ways. The percentage of nitrogen and of iodine in every specimen agreed accurately with those required by the formula.

Moreover, all attempts to prepare similar bodies of a different composition in aqueous solution completely failed.

It may be taken, therefore, as a definitely proved fact that only one compound of the nature of nitrogen iodide has ever been prepared in aqueous solution, and that the composition of this is represented by the empirical formula $N_2H_3I_3$.

It is as certain as any inference can be that the discordant numbers of previously published analyses are due to three causes: unsuitable analytical methods, in which a variable amount of gaseous nitrogen was liberated and escaped estimation; decomposition by light during manipulation, and loss of the free nitrogen thus produced; and decomposition by prolonged washing, with liberation and consequent loss of ammonia. These adequately account for the varying results observed, because in every previously recorded analysis except a single one made by Bunsen (which agrees very nearly with the author's results) less than two atoms of nitrogen have been found associated with three atoms of iodine as would be the case if any or all of these causes were operative. Since single analysis only have, as a rule, been made of specimens prepared in different ways, chemists have concluded that they had in their hands distinct but similar substances of definite composition. Mixtures of any composition from nitrogen iodide, $N_2H_3I_3$, to pure iodine can, in fact, be obtained by washing nitrogen iodide continuously, and might be assumed in the absence of any evidence to the contrary to be definite substances.

There is so far very little direct evidence from which to deduce a constitutional formula for the compound. It may be supposed with a fair degree of certainty that the two

nitrogen atoms are linked together, and all the evidence we have goes to show that the formula $NH_3 = NI_3$ is probably the correct one.

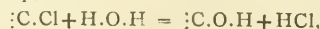
Nitrogen iodide which has been washed with water for a considerable time becomes more liable to explode, and analyses of such partly decomposed material point to a decomposition of the molecule and a liberation of very unstable NI_3 in the residue. The latter compound cannot, however, be isolated, and only appears to exist in presence of a large excess of free iodine; it is probably formed by the molecule $NH_3 = NI_3$ breaking down in the first instance into NH_3 and NI_3 , the ammonia being washed away either alone or combined with hydriodic acid,* leaving the NI_3 as an insoluble residue mixed with iodine and still undecomposed nitrogen iodide.

The view that the constitution of the so-called "nitrogen iodide" is represented by the formula $NH_3 = NI_3$ is supported to a certain extent by the recent work of Hugot, who found that when iodine was placed in excess of anhydrous liquefied ammonia, it dissolved, and deep green needle-shaped crystals were deposited, whose composition was represented by the formula $3NH_3.NI_3$. Kept at -30° C. in a vacuum, these crystals lost a molecule of ammonia, and left a brass-yellow crystalline body having the composition $2NH_3.NI_3$; this latter substance, exposed in its turn at 0° in a vacuum, lost another molecule of ammonia and gave ordinary nitrogen iodide, $NH_3 = NI_3$.

The formula has lately received further confirmation from the observation of Silberrad, that a small quantity of triethylamine is produced when nitrogen iodide suspended in ether is acted upon by zinc ethyl.

During the past few years much work has been done on substituted nitrogen chlorides and bromides, classes of compounds previously little known, and the knowledge gained enables us to formulate the behaviour of nitrogen iodide very clearly.

A halogen atom attached to nitrogen behaves in a characteristic way on hydrolysis wholly different from the way it behaves when attached to carbon. In the latter case the halogen atom is replaced by hydroxyl, being itself removed in combination with hydrogen, in the former it is invariably replaced by hydrogen, itself uniting with the hydroxyl group, thus—



All reactions of nitrogen iodide, therefore, carried out in presence of water may be formulated as if the nitrogen iodide first became hydrolysed into ammonia and hypiodous acid, $NH_3.NI_3 + 3HOH = 2NH_3 + 3HOI$, the latter then interacting in its own characteristic manner.

The reactions of nitrogen iodide are, however, complicated by the circumstance that a partial breaking down of the compound into nitrogen and hydrogen iodide almost invariably accompanies the main reaction. This secondary reaction, $NI_3.NH_3 = N_2 + 3HI$, takes place to a greater or less extent according to the nature of the main reaction and the conditions under which it is taking place, and is especially promoted by the influence of light. Since hydrogen iodide reacts at once with hypiodous acid, liberating iodine, the latter element is nearly always set free when the nitrogen iodide enters into any chemical action. This circumstance, coupled with its explosive nature, has caused all the difficulty which has been experienced in its investigation.

To Purify Drinking-water.—M. Lambert proposes to add 6 c.grms. of permanganate of potash to each litre, and, ten minutes after, 10 c.grms. of manganese sulphate. After precipitation carefully decant.—*Chemist and Druggist.*

* The hydriodic acid is formed by a secondary decomposition, identical with that which takes place under the influence of light, which occurs to a small extent; the nitrogen simultaneously formed escapes as gas. The iodine is set free by the action of this hydriodic acid upon a further portion of the nitrogen iodide.

THE QUANTITATIVE DETERMINATION OF CARBON DIOXIDE AND OF CARBON.

By JOHN McFARLANE and ARNOLD W. GREGORY.

IN the determination of small percentages of carbon or of carbon dioxide, the absorption of the latter in weighed potash bulbs is unsatisfactory on account of the small increment of weight. Thus, as A. A. Blair points out ("Chemical Analysis of Iron," p. 148), "in damp weather it is almost impossible to get good results, the condensation of moisture on the absorption apparatus rendering the weighing extremely difficult, even when the utmost care is taken." Our own experience in the determination of carbon in steels of low carbon content fully bears out Blair's remark.

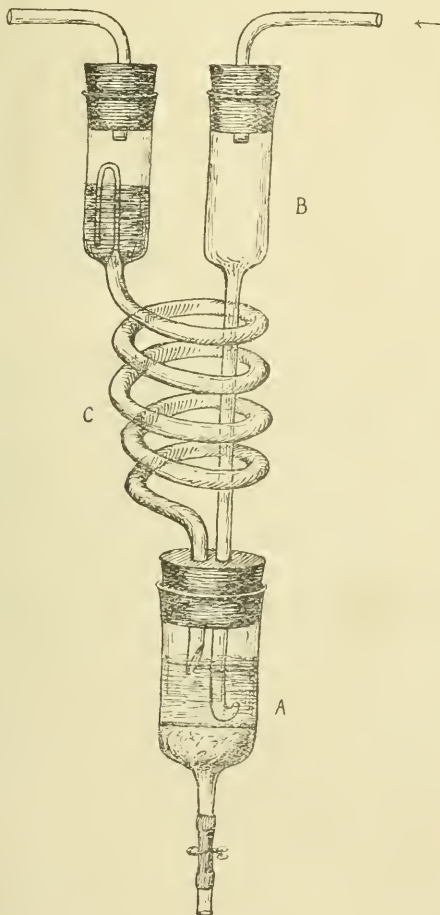


FIG. 1

The following example makes the difficulty apparent:—Three grms. of steel were burned by the direct combustion method, and the carbon dioxide absorbed in a weighed potash bulb. The increase in weight was 0.0110 gm., equivalent to 0.10 per cent carbon. A difference of 1 m.grm. in the above weight would cause an error to the extent of about 10 per cent of the carbon present.

This fact led us to adopt the barium hydrate absorption method, first proposed by Pettenkoffer.

The advantage of this method of absorption lies in the

fact that 197.4 parts of barium carbonate are formed from 12 parts of carbon, whereas only 44 parts of carbon dioxide are produced from a similar amount of carbon.

Moreover, as Dupré and Hake have shown (*Journ. Chem. Soc.*, xxxv., 1159) the barium carbonate, which is only removed from the absorption apparatus with difficulty, may be dissolved in hydrochloric acid, and finally converted into barium sulphate, 233.46 parts of which correspond to 12 parts of carbon.

At the same time there will be a loss of alkalinity in the filtrate from the barium carbonate, so that by using a measured quantity of barium hydrate solution of known strength and titrating the filtrate after absorption of CO_2 with standard acid solution, the amount of carbon or carbon dioxide may be calculated. This gives two methods for determining carbon or carbon dioxide in a single absorption.

There are two chief difficulties, however, in using barium hydrate solution; first, a large volume of the solution is required on account of the sparing solubility of barium hydrate, and thus a cumbersome absorption apparatus must be used; secondly, during the process of filtration carbon dioxide may be absorbed from the atmosphere, which fact constitutes a serious disadvantage of the method.

In order to overcome the second difficulty, F. A. Gooch and K. Phelps (*Zeit. Anorg. Chem.*, 1895, ix., 356–359) use a layer of xylene on the surface of the barium hydrate solution.

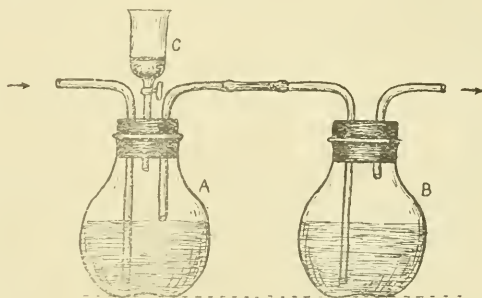


FIG. 2

By using the apparatus about to be described this is unnecessary, since filtration takes place in an atmosphere freed from carbon dioxide. Efficient absorption is produced by the prolonged contact of the gas with a minimum volume of liquid. Filtration and absorption take place in the same apparatus.

Fig. 1 consists of a wide filter-tube, A, closed by a small piece of rubber tubing and a clip. A plug of glass-wool is inserted into the base of the wider part, and covered by a layer of paper or asbestos pulp. It is advisable to cover the pulp with a little broken glass, which serves to keep it in position during the agitation of the liquid caused by the passage of the gas. The mouth of the filter-tube is closed by a rubber stopper with two holes, through one of which passes a glass tube, B, bent and constricted at its lower end, and enlarged at its commencement as shown in Fig. 1.

Through the second hole a spirally bent tube, C, is placed, which terminates in the same form as the inlet tube B commences, except that a small inverted U-tube is fused inside.

Before making a determination, air, freed from carbon dioxide, is passed through the apparatus, which is connected to the combustion tube or evolution flask. When all carbon dioxide is removed, the rubber stopper in the mouth of B is taken out, and a measured quantity of the barium hydrate solution introduced. The liquid now fills the filter-tube, A, and partially fills the spiral, C. The stopper in B is now replaced, and the current of air once more passed in, whereupon some of the liquid from the spiral is carried

over through the small inverted U-tube into the enlarged termination of c.

The determination is now commenced. Carbon dioxide passes through B, then on to A, where absorption chiefly takes place, and finally the last traces of the gas are retained in the spiral. The barium hydrate in the termination of c should remain clear if absorption is complete in the spiral, but unless care is taken barium carbonate will be carried mechanically through the small U-tube.

When all the carbon dioxide is absorbed, the clip on A is opened, and the filtrate collected. The barium hydrate is washed out of the apparatus with boiling water to which a few drops of phenolphthalein solution have been added, the washing being discontinued when the filtrate only shows a very faint pink colour. The filtrate and washings are mixed, and the solution titrated with N/10 H_2SO_4 , and the carbon or carbon dioxide calculated from the loss of alkalinity of the barium hydrate.

The barium carbonate in the apparatus is dissolved in very dilute hydrochloric acid, and converted into barium sulphate, filtered, ignited, and weighed.

From the weight of barium sulphate the carbon or carbon dioxide may be calculated. We obtained excellent results with this apparatus in the determination of small quantities of carbon dioxide, but in dealing with larger quantities the barium carbonate formed being gelatinous in nature, and large in quantity, rendered filtration difficult, and the precipitate appeared to occlude a trace of barium hydrate, since the results obtained were very slightly but consistently high; this effect, however, being minimised by the large amount of barium sulphate derived from a small amount of carbon.

Thus in an extreme case the weight of barium sulphate was 10 m.grms. in excess of that demanded by theory, giving an excess of 0.5 m.grm. of carbon over the amount present.

In working with very large amounts of carbon dioxide the difficulty of filtration is so great as to render the method impracticable, and also in this case the efficiency of absorption is limited by the sparing solubility of barium hydrate.

Another method which we have used consists in absorbing carbon dioxide in an ammoniacal barium chloride solution, when soluble barium carbamate is formed, which, however, is unstable, so that a slight precipitation occurs even in the cold. On warming, the precipitate of barium carbonate increases, and at the boiling-point a quantitative yield is obtained.

Barium carbonate thus differs from calcium carbonate in being completely precipitated on boiling in presence of ammonia, as E. Divers (*Journ. Chem. Soc.*, xxiii., 230 and 360) states that caustic ammonia in presence of excess of calcium chloride very considerably retards the precipitation of calcium carbonate, and Drechsel (*Fourn. Prakt. Chem.*, [2], xvi., 180—200) finds that calcium carbonate is not completely decomposed on prolonged boiling in presence of ammonia. Fresenius describes this method ("Quantitative Chemical Analysis," vol. i., p. 332, English edition), and concludes that it is not capable of giving good results unless numerous precautions are taken.

Thus, Fresenius recommends that, after the absorption of the carbon dioxide, the ammoniacal barium chloride be heated for one and a-half to two hours in a tall vessel of water at 98° C., since active ebullition would occasion loss of ammonium carbonate, due to the action of ammonium chloride on the precipitated barium carbonate. The hot solution is then filtered.

Our experiments show that precipitation of barium carbonate is complete after boiling for one minute, and that the action of the ammonium chloride on the barium carbonate is so slight as to be negligible.

The following experiment proves the correctness of the first statement:—Carbon dioxide was passed into an ammoniacal barium chloride solution, so that the latter still remained in considerable excess. The solution was then boiled for one minute, and filtered into a flask through

which air freed from carbon dioxide was passing. The solution was then heated for an hour. No precipitation occurred.

Instead of filtering the hot solution, we first allow it to cool, and then filter, so that any carbon dioxide which is absorbed from the atmosphere during the process forms the soluble carbamate, and passes into the filtrate, whereas on filtering the hot solution, barium carbonate is formed from atmospheric carbon dioxide, and causes the result obtained to be too high. By proceeding in this manner we eliminate the error which arises from the absorption of atmospheric carbon dioxide, the chief difficulty in the use of barium hydrate for the absorption of carbon dioxide.

The solution of barium chloride contains 50 grms. BaCl_2 and 250 c.c. ammonia solution (specific gravity 0.880) per litre. In carrying out a determination the ammoniacal barium chloride solution was boiled and filtered into two small flasks, as shown in Fig. 2. C is a filter-tube containing glass-wool covered with asbestos pulp. The exit tube of A is of such a length as to allow the solution to pass over into B when A is half full. Air freed from carbon dioxide is passed through the flasks before the liquid enters.

The greater part of the carbon dioxide is absorbed in the first flask, and the remainder is retained by the second. When the absorption is finished, the flask A is heated (whilst still in connection with the combustion tube) until it commences to boil. The steam generated passes over into B, and both flasks are thus heated to the desired temperature. The flasks are then cooled, and removed from the other part of the apparatus, and the BaCO_3 filtered off (a similar filter being used as in the flask A), washed with cold, and finally with hot water.

The barium carbonate on the filter is dissolved in dilute hydrochloric acid, as also any which may have remained on the walls of the absorption flasks and tubes. The solution is boiled and dilute sulphuric acid added, the barium sulphate being precipitated in a granular form, and may be filtered within five minutes of precipitation.

Though the operations involved take a rather longer time than those necessary in the case of absorption by potash, they are simple in nature, and the greater accuracy attainable quite justifies the lengthened process.

We have used this method in the estimation of carbon dioxide in carbonates, and of carbon in steel.

On testing the method, a small quantity of powdered calc spar was weighed in a porcelain boat, and heated to redness in a porcelain combustion tube through which a stream of air freed from carbon dioxide was passed. The tube was allowed to cool, and the boat removed and weighed. The loss of weight gave the weight of carbon dioxide evolved.

Example 1.—0.2153 grm. CO_2 gave 1.1400 grm. BaSO_4 .

The weight of carbon dioxide, calculated from the above weight of barium sulphate, is 0.2148 grm.

Example 2.—0.3832 grm. CO_2 gave 2.0350 grm. BaSO_4 .

Calculated, CO_2 , 0.3835 grm.

The accuracy of the method for the determination of small quantities of carbon dioxide is shown by the following experiment:—0.0265 grm. of sodium carbonate was dissolved in hydrochloric acid and the carbon dioxide absorbed.

Weight of BaSO_4 obtained ..	0.0597 grm.
Weight of carbon calculated ..	0.00307 "
Theoretical weight of carbon ..	0.00300 "

Copper Steels.—Pierre Breuil. — The author has already investigated copper steels containing 0.15 to 0.38 per cent of carbon, and he now continues his researches to those containing 0.56 to 0.79 of carbon, and gives a series of tables of his results which show the apparent limit of elasticity, stretching power, &c.—*Comptes Rendus*, clxiii., No. 7.

NOTICES OF BOOKS.

Lecture Notes on Chemistry for Dental Students. By H. CARLTON SMITH, Ph.G. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1906.

THE author of this book has a high ideal regarding the knowledge of chemistry which a dentist should possess, and though probably but few students will come up to this ideal, the use of his book can be recommended for all. It follows the lecture course in dental chemistry as given by Dr. Smith at the Harvard Dental School, and gives full directions for the appropriate practical work. The student is supposed to have had some elementary training in chemistry, both theoretical and practical, and begins his dental course with qualitative analysis. This first part of the book has many good features; for instance, the recognition of the importance of always using solutions of known strength. Then dental metallurgy is taken up, including the chemistry of alloys, amalgams, solders, and cements, directions being given for their preparation. Volumetric and micro-chemical analysis are both very shortly treated, the latter subject being illustrated by a few plates showing the crystals most frequently met with or best suited for the study of micro-chemical processes. The examination of teeth and tartar is then discussed sufficiently fully, while organic and physiological chemistry are given their full share of space, and the student who works through and assimilates the last two sections of the book should be particularly well equipped to understand the problems of dentistry.

August Wilhelm von Hofmann. By BERNHARD LEPSIUS. Leipzig: Duncker and Humblot. 1905.

THE life of August Wilhelm von Hofmann has a special interest for English men of science, on account of the important part he played in spreading a knowledge of chemistry in this country while he was Professor at the College of Chemistry, which has sent out numbers of eminent men, many of whom happily are still living. This biography narrates the chief events in the great chemist's life, and gives an excellent account of his many-sided activity, describing shortly the researches which have made his name so universally known. Special stress is laid on those which have important practical applications; for example we need only mention the work on the aniline dyes (in which Perkin was his assistant) and on formaldehyde, which so long eluded preparation in the pure state, and which is of such great biological and hygienic importance. Allusion is also made to Hofmann's literary work and his share in the formation of the Deutsche Chemische Gesellschaft, while a clear picture is given of his charming personality, which won for him so many friends, both in England and on the Continent, and a tribute is paid to his enthusiasm as a teacher and to the generosity with which he placed all the help and encouragement in his power at the disposal of those who came in contact with him.

Handbuch der Anorganischen Chemie. ("Manual of Inorganic Chemistry"). Edited by Dr. R. AEBEGG. Vol. III., Part I. Leipzig: S. Hirzel. 1906.

THE first part of Volume III. of this valuable text-book contains the elements of Group III., namely, boron, gallium, indium, and thallium, and the rare earths. It still preserves its high reputation for comprehensiveness and special attention to physical chemistry, and when it is said that Prof. Brauner is responsible for a large part of the volume, including the chapters on the atomic weights, it will not be necessary to comment further upon the thoroughness and general excellence of the book. The critical discussions of the literature of the elements of the rare earths constitute a special feature, and the particularly complete treatment of these elements would alone be sufficient to recommend the text-book very highly as a work of reference.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 6, August 6, 1906.

Iodomercures of Sodium and Barium.—A. Duboin.—The author prepares sodium iodomercurate, $2\text{NaIHgI}_2 \cdot 4\text{H}_2\text{O}$, a salt which is extremely deliquescent. He also prepares a new iodomercurate of barium by leaving a solution of mercuric iodide in barium iodide (having composition—Barium, 12.45; mercury, 22.53; iodine, 51.68; and water, 13.34 per cent) to evaporate very slowly in dry air through the heat of summer. Enormous crystals are deposited, of density 4 and formula $\text{BaI}_2 \cdot \text{HgI}_2 \cdot 5\text{H}_2\text{O}$. The other properties of this salt are very much the same as those of the barium salts which the author has described in a previous paper.

Alkaline Earth Boro-stannates. Reproduction of Nordenskiöldine.—L. Ouvrard.—The author's researches on the metallic borates led him to investigate the different methods of obtaining the alkaline earth boro-stannates, of which there exists one natural example, Nordenskiöldine (calcium boro-stannate). He obtains the best results by mixing precipitated borate of lime, of formula $\text{CaO} \cdot 2\text{B}_2\text{O}_3$, with a quantity of tin dioxide in a platinum boat; the latter substance being prepared by the calcination of metastannic acid. The boat is then heated to redness in a porcelain tube through which a current of hydrochloric acid slowly passes. After treating the mass thus obtained with acidulated water, &c., the boro-stannate, $\text{B}_2\text{O}_3 \cdot \text{SnO}_2 \cdot \text{CaO}$, is isolated. This substance is in the form of colourless, transparent, almost infusible crystals, which are unattacked by concentrated hydrochloric acid.

Influence of the Temperature of Dehydration of Gypsum on the Hardening Power of the Plaster obtained.—E. Leduc and Maurice Pellet.—Hitherto no experiments have been made on the influence of the temperature of dehydration of gypsum on the setting power of the plaster obtained. The authors dehydrate gypsum at various temperatures, and then determine the curve obtained by testing the plasters thus prepared by means of a Périn tester. One of the most interesting results obtained is that, when alabaster is dehydrated at 450° no sensible rise of temperature takes place during the setting of the plaster, but if the dehydration takes place at 250° there is a decided rise of temperature (15.5° in twelve minutes approximately).

MISCELLANEOUS.

Schools of Chemistry.—The following additional information has been received:—

NORTHERN POLYTECHNIC INSTITUTE, Holloway, N.—Principal, R. S. Clay, D.Sc.; Head of the Chemical Department, W. H. Mills, M.A., Sc.D.; Assistants, W. H. Watson, B.Sc., A.R.C.S., Miss A. M. Bain, M.A., B.Sc., and F. W. Linch. Instruction in Theoretical and Practical Inorganic and Organic Chemistry, Systematic courses for London University Degrees, Pass and Honours, and Board of Education examinations. Session begins September 17. Prospectus free on application to the Secretary.

NORTHAMPTON INSTITUTE, St. John Street, E.C.—Principal, R. Mullineux Walsley, D.Sc., F.R.S.E., &c. Chemistry: Messrs. S. Field, A.R.C.S., E. B. Ware, A. H. Munday, F.C.S., G. Naylor, F. Edwards. Evening Courses in Elementary, Applied, and Engineering Chemistry, and Electro-chemistry, Electro-plating, Electro-metallurgy, &c. Day and Evening Courses in Engineering (Mechanical and Electrical), Technical Optics, Artistic Crafts, and Horology. The classes of the Day Courses commence on Monday, October 1st, and those of the Evening Courses on Monday, September 24th. Full details of the syllabuses in the various subjects and the equipment and special developments for the forthcoming session may be obtained on application to the Principal.

Appointments.—Dr. Morris W. Travers, F.R.S., Professor of Chemistry at University College, Bristol, has been appointed Director of the Indian Institute of Science which is to be established at Bangalore. The Council of University College, Bristol, have offered the vacant Chair of Chemistry to Dr. Francis Francis, D.Sc., Ph.D., F.I.C. Dr. Francis studied at University College, Liverpool (now the University), and at Erlangen, and has been Assistant Professor at University College, Bristol, since 1903. He obtained the degree of D.Sc. for researches in organic chemistry, and has published many papers in journals of chemical societies both in England and Germany.

BOROUGH OF SOUTHWARK.

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Canvassing will disqualify.

J. A. JOHNSON,
Town Clerk.

Southwark Town Hall,
Walworth Road, S.E.,
September 12, 1906.

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The Council does not bind itself to accept the lowest or any Tender, and it will not accept the Tender of any person or firm who shall on any previous occasion have withdrawn a Tender after the opening of the same, unless the reasons for the withdrawal were satisfactory to the Council.

G. L. GOMME,
Clerk of the London County Council.

The County Hall, Spring Gardens, S.W.,
September 6th, 1906.

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THE CHEMICAL NEWS.

VOL. XCIV., No. 2443.

OXIDATION IN SOILS AND ITS RELATION TO PRODUCTIVENESS.*

By FRANCIS V. DARBISHIRE, B.A., Ph.D.,
and
EDWARD J. RUSSELL, D.Sc.

ALL soils possess the power of absorbing oxygen, some to a marked extent. The authors have devised an apparatus for measuring the rate of absorption, and they have studied the influence of various factors and also the connection with the productiveness of the soil.

It has been found that oxidation is mainly, but not entirely, due to the activity of micro-organisms; oxidation still goes on in soil sterilised at 120° C. or by treatment with 1 per cent mercuric chloride, but the rate is only about one-fifth of what it was.

The rate of oxidation does not entirely depend on the amount of organic matter present in the soil. Moisture is essential; as its amount increases, the rate of oxidation also increases, until near the point at which the soil becomes waterlogged. The addition of calcium carbonate or of food, *e.g.*, sugar, increases the rate. In the latter case the maximum increase occurs with 1 per cent of sugar. Small quantities of poison like mercuric chloride, thymol, copper sulphate, &c., also increase the rate till the optimum amount, 0.01 per cent, is reached; further quantities bring the rate down considerably.

Somewhat different results were obtained with partially sterilised soils. If a soil is exposed to vapours of chloroform, carbon disulphide, or toluene, and the antiseptic then removed in a current of air, the rate of oxidation markedly increases. A similar result follows when the soil has been exposed to a temperature of 85° C., insufficient to kill spores.

The rate of oxidation is closely parallel to the productiveness of the soil. For a series of similar soils, of which the cropping power is known, it is found that the most productive has the highest rate of oxidation, and that the others follow in the same order for both properties. The parallelism holds, not only for soils in the natural state, but also, with certain limitations, for soils which have been artificially treated. Thus, partial sterilisation by heating to 95° increases the rate of oxidation and also increases the productiveness for non-leguminous plants; treatment with volatile antiseptics has the same result. It is essential, however, that the soil conditions should be aerobic, as in arable soils; pasture soils, where the conditions are anaerobic, do not show the same relationship. In view of this difference the authors suggest that the rate of oxidation affords a measure of the bacterial activity, which is closely connected with productiveness.

RESEARCHES ON HIGH PERCENTAGE OZONE GAS.†

By ERICH LADENBURG, Ph.D.

THE research which I have the honour to bring before you has been made in the Physical Laboratory of Professor Rubens, together with Dr. Erich Lehmann, assistant of Professor Miethe.

Four years ago E. Goldstein described a method of making pure liquid ozone. He put pure oxygen into a

* Abstract of a Paper read before the British Association (Section B), York Meeting, 1906.

† A Paper read before the British Association (Section A), York Meeting, 1906.

vacuum tube under a pressure of 3 to 5 c.m., and allowed the discharge of a small induction coil to pass through the gas. Under the influence of the ultra-violet light of this discharge the oxygen is changed into ozone, and by cooling the tube with liquid air this ozone becomes liquefied; the pressure in the tube falls to one-twentieth of a millimetre; that is, to the pressure of liquid ozone of that low temperature. Continuing this process one gets 2 c.c. of liquid ozone in one hour.

By allowing this liquid ozone to vaporise into a vacuum tube, it ought to be possible to get pure, or nearly pure, ozone gas. We have made this experiment, and could confirm the above-mentioned supposition. We obtained a gas which had a dark-blue colour in 30 c.m. thickness under a pressure of 200 m.m. In examining the absorption spectrum of this gas we hoped to get more accurate results than previous observers, who could only use an 8 percentage ozone for their researches. Among these scientists, Chappuis examined the visible, Hartley the ultra-violet, and Angstrom the infra-red part of the absorption spectrum of ozone.

We used the following methods of observation:—In the ultra-violet part we photographed the absorption spectrum with a quartz spectrograph, and measured the absorption bands on the photographs. In the visible part we also photographed, or we used an ordinary spectrometer. In the infra-red we made use of a mirror spectrometer with thermopile and galvanometer. In the ultra-violet we used quartz as the prism and for closing our ozone tubes, and in the infra-red rock-salt.

Burning magnesium ribbon was employed as the source of light for the ultra-violet, incandescent gas for the visible, and a Nernst lamp for the infra-red part. For measuring the pressure in the ozone tube, we could not use an ordinary gauge, because ozone immediately attacks all metals. Therefore we tried to blow a glass gauge similar to the metallic gauge which was used by Bourdon. We obtained an instrument with which we could accurately measure the half of a millimetre of pressure.

The following are the results of our researches on the absorption spectrum of ozone:—

In the ultra-violet ozone has a very peculiar kind of absorption. If the proportion of ozone is very small, we find in harmony with the results of previous observers an absorption commencing in the ultra-violet and reaching to 0.31 μ . With a larger proportion of ozone a great number of new bands appear at the ultra-violet end of that part of the spectrum, which previously did not exhibit any absorption bands. The more the amount of ozone increases the more these bands appear in the region of longer waves and become enlarged until the whole of this part of the spectrum is absorbed.

In the visible part of the spectrum we found fourteen absorption bands, and besides these bands we got a great weakening of the red end of the spectrum extending to 0.50 μ . And we believe this weakening is the cause of the blue colour of ozone gas.

In the infra-red we found a great number of absorption bands, the largest of which lies between 9 and 10 μ , and here ozone absorbs nearly 100 per cent.

In liquid ozone, which we also examined, we did not find any absorption bands, but only a great weakening of the red end of the spectrum. This is the cause of its blue colour.

Besides the above-mentioned absorption bands we found five new ones in the visible red part at the following points of the spectrum, namely,—

670—667, 638, 628, 622, and 610 μ .

The existence of these bands confirmed a supposition which I had drawn a year ago in order to explain peculiar results obtained when examining the ratio of the two specific heats of ozone. I obtained numbers which were too small for a triatomic gas. I was consequently compelled to assume there must be another body present in the ozone.

These five bands showed quite different properties from

the ozone bands. They only appeared after the greater part of the ozone was vaporised, and they disappeared very soon. First we thought that these bands also belonged to the ozone and did not become visible until a certain degree of pressure had been reached. But this was proved not to be the case, as we obtained these bands even when we had only a very small quantity of ozone, and, on the other hand, we always observed an increase of pressure in connection with their disappearance. Therefore they must belong to another body, and we tried to separate this unknown body from the ozone. For that purpose we used a second absorption tube which we could shut off from the first by a tap. At the moment in which we saw the new bands appearing in the first tube we closed this tube and allowed the rest of the liquid to vaporise into the other tube. And here we found the new bands without the ozone bands. Therefore it was proved that they belonged to a new body. We had made the liquid ozone by an oxygen which was developed by electrolysis of boiled potassium hydrate, and the whole apparatus was exhausted as far as possible before beginning with the experiments. Therefore we excluded the presence of nitrogen as well as that of other impurities. And consequently we have to believe that this body, which the five new bands belong to, is a third modification of oxygen, and this being the case it must have more atoms in its molecule than ozone, because the pressure increases with the disappearance of this body. The amount of the increase of pressure was so great that it seemed to be possible to prove our opinion by an examination of the specific gravity of the gas which vaporised from the liquid ozone. We measured volume, weight, pressure, and temperature of the gas, and obtained the following six results for its specific gravity:—

1·738, 1·832, 1·751, 1·768, 1·737, 1·840,

the average being 1·774.

The specific gravity of the triatomic ozone would be—

1·661.

It is not very easy to work with pure ozone, and especially with this new body, because they are very explosive, and we could not yet determine the conditions of these explosions.

Therefore we have only examined very few properties of the new body. But the following is certain:—

It has a higher boiling-point than ozone, it has more atoms in its molecule, it is of a dark blue colour, whether liquid or gaseous, and it is not very stable at the ordinary temperature.

A METHOD FOR DETERMINING VELOCITIES OF SAPONIFICATION.*

By Professor JAMES WALKER, F.R.S.

A POSSIBLE method of following the progress of a reaction in which electrolytes are involved is to measure the electrical conductivity of the solution at stated intervals. This method was employed by Walker and Kay in their investigation of the conversion of ammonium cyanate into urea, and is capable of a more extended application (*Journ. Chem. Soc.*, 1897, lxxi., p. 489).

The chief conditions for the convenient application of the method are:—First, that there should be a considerable difference in conductivity between the initial and final systems; and, second, that the change in conductivity should be proportional to the progress of the reaction. It occurred to me that these conditions would be well fulfilled in the saponification of an ester by a caustic alkali. The conductivity of the alkali—say sodium hydroxide—is much greater than that of the sodium salt produced by the saponification, owing to the high velocity of hydroxidion as compared with the salt anion. Since, too, sodium hydroxide and sodium salts of monobasic acids are approxi-

mately equally ionised under the same conditions, the ionisation in dilute solution remains practically the same throughout the saponification, and thus the alteration in the conductivity is almost exactly proportional to the progress of the reaction.

The following experiment on the rate of saponification of methyl acetate by caustic soda may be quoted as an example of the method carried out under ordinary laboratory conditions with the apparatus generally used for conductivity measurements in solution.

The conductivity cell used was of the narrow Arrhenius type, and was immersed in a thermostat at 25°. In this cell were placed 4 c.c. of N/20 caustic soda and 15 c.c. of water. To prevent access of carbon dioxide, the hole in the ebonite cover was plugged with a small rubber stopper. When the temperature of the thermostat had been reached, the solution was stirred by raising and lowering the electrodes, and the conductivity was read off. To the solution was then added 1 c.c. of N/5 solution of methyl acetate, the time being simultaneously noted, and the contents of the cell were well stirred by up and down motion of the electrodes. A reading of the conductivity was at once taken after mixing, but this acted merely as a check, and was not used in the calculation. After a short interval readings were made of the conductivity of the solution (which was now N/100, both with regard to sodium hydroxide and to methyl acetate), at first every minute, and then every few minutes when the reaction had become slower.

The following table contains the results of the observations. In it a represents the bridge reading and x the difference between the initial value of $a/(1-a)$, which is proportional to the conductivity, and the value after t minutes.

t .	$a/(1-a)$.	x .	$\frac{1}{t} \cdot \frac{x}{1-x}$.
0	(1·564)	0	—
3	1·304	0·260	0·117
4	1·247	0·317	0·116
5	1·198	0·366	0·115
6	1·153	0·411	0·116
7	1·114	0·450	0·117
8	1·083	0·481	0·116
10	1·026	0·536	0·115
12	0·980	0·584	0·117
15	0·927	0·637	0·117
18	0·883	0·681	0·118
21	0·852	0·712	0·118
25	0·818	0·746	0·118
∞	(0·564)	(1·000)	Mean 0·118

It will be noticed that the constant for the bimolecular reaction is here very satisfactory, and in general it may be said that the maximum divergence from the mean value does not exceed 1 to 2 per cent. It is, however, advisable to neglect the first and last fourths of the reaction, since in them initial disturbances and the effect of a slight departure from exact equivalence of the reacting substances have a relatively large effect on the value of the constant.

The initial reading of the conductivity cannot be taken directly, owing to the great speed of the reaction. In order to obtain it, the conductivity of the alkaline solution is read before the methyl acetate is added. In the above instance the conductivity read in this way is that of a solution N/95 with regard to sodium hydroxide, 4 c.c. of N/20 solution being contained in 19 c.c. When this is diluted to N/100 by the addition of 1 c.c. of the methyl acetate solution, the conductivity will fall off in the ratio of 100 to 95, since the quantity of methyl acetate in the solution after mixing is less than 0·1 per cent, and can have no appreciable effect either on the speed or the number of the ions. From the conductivity of the solution before addition of the methyl acetate we therefore deduct one-twentieth of its value in order to obtain the initial conductivity after mixing.

* A Paper received by the Royal Society, July 10, 1906. From the Chemical Laboratory, University College, Dundee.

The final reading may, of course, be ascertained by waiting till the action has ceased, but it is both more expeditious and more accurate to measure the conductivity of a N/100 solution of sodium acetate prepared by neutralising the N/20 solution of caustic soda by means of acetic acid and diluting to the requisite extent. It is well to make this measurement of the end-point before beginning the actual saponification. Theoretically the end-point can be calculated from the initial reading and the known ratio of the conductivities of N/100 solutions of sodium hydroxide and sodium acetate, but it is advisable to perform the experiment as a check.

The calculation of the constant $\frac{1}{t} \cdot \frac{x}{1-x}$ may be simplified by the following device:—For conductivity work a table is used which gives the ratio $a/(1-a)$ for different values of the bridge-reading a . If, therefore, we make the total range of the reaction equal to unity, we can use the same table to obtain the ratio $x/(1-x)$ and have then merely to divide by the time, t ,—a calculation which can be performed mentally if the intervals are suitably chosen. Now it is always possible to make the range between the initial and final values of $a/(1-a)$ equal to unity by introducing the appropriate resistance in the resistance box. Thus, in the above example, it was found that the ratio between the initial and final conductivities was 2.773 : 1. We have, then, $i/f = 2.773$, and we wish to make $i-f = 1$. From these two equations we obtain $i = 1.564$ and $f = 0.564$. We have therefore so to adjust the resistance that the initial value of $a/(1-a)$ shall be 1.564. This refers to the N/100 solution after mixing, whilst the conductivity actually measured is that of a N/95 solution. We must therefore increase the value 1.564 in the ratio of 100 to 95, and thus obtain 1.646 as the value of $a/(1-a)$ which the N/95 solution of caustic soda must exhibit if the difference between the initial and final values of $a/(1-a)$ is to be unity. In the table this value of $a/(1-a)$ corresponds to $a = 0.622$. We therefore adjust the resistance in the box, either by trial or by calculation, until the minimum for the N/95 solution of caustic soda is exactly at this part of the bridge, and then proceed with the experiment. This adjustment, though tedious in description, only occupies a few minutes in practice, and saves much time in the subsequent calculations. Even if readings are taken every minute, the calculation of the constant $\frac{1}{t} \cdot \frac{x}{1-x}$ from each observation can be performed in the interval between two readings, generally without the necessity of putting pen to paper.

To obtain the velocity constant from the mean value of $\frac{1}{t} \cdot \frac{x}{1-x}$ it is only necessary to divide by the normality of the solution. In the above instance the velocity constant is thus $0.117 \div 0.01 = 11.7$.

As a further example of the method, I append a series of observations made by Mr. D. C. Crichton, B.Sc., on the velocity of saponification of ethyl acetate by caustic soda at 24.85°, the concentration of both substances being N/100.

t .	$a/(1-a)$.	x .	$\frac{1}{t} \cdot \frac{x}{1-x}$.
0	(1.560)	0	—
5	1.315	0.245	0.0649
7	1.247	0.313	0.0651
9	1.193	0.367	0.0645
11	1.146	0.414	0.0642
13	1.101	0.459	0.0652
15	1.064	0.496	0.0650
18	1.020	0.540	0.0652
20	0.994	0.566	0.0652
25	0.945	0.615	0.0642
27	0.923	0.637	0.0650
33	0.880	0.680	0.0644
37	0.756	0.704	0.0644
∞	(0.560)	(1.000)	Mean 0.0647

The velocity constant of the saponification of ethyl acetate by caustic soda at this temperature is therefore 6.47, a value in exact accordance with the curve which expresses the results of Warder (*Am. Chem. Journ.*, 1881, vol. iii., p. 203) and of Reicher (*Liebig's Annalen*, 1886, vol. cxxxii., p. 103) obtained by the titration method.

The conductivity method, even without special apparatus, is at least as accurate as the titration method carried out under specially favourable circumstances, and for rapid reactions is incomparably less trying in execution.

ORE DEPOSITS AND THEIR DISTRIBUTION IN DEPTH.*

By Prof. JOHN W. GREGORY, D.Sc., F.R.S.

PRIMITIVE man obtained his limited store of metal by gathering scanty grains and pebbles of ore from the beds of streams; but even in pre-historic times he worked shallow mines, for Job tells us that the gold miners of his day not only diverted rivers from their courses, as in modern alluvial practice, but they put forth their hands upon the flinty rock, by which he doubtless meant quartz. Still less do alluvial ores satisfy modern requirements, even though the great metal-using countries place the rest of the world under tribute of its mineral wealth; and owing to the exhaustion of the richer ores in the more accessible mining fields, miners are now thawing the frozen gravels of Klondike, washing the gold-bearing loams in the Siberian rivers during their short summer flow, mining in the malarial jungles of West African coast lands, and sluicing low grade drifts in the heart of Africa, in Katanga.

We cannot expect many more discoveries of alluvial deposits as rich and as extensive as those of California and Australia; nor can we go back to the low metal output of a century ago. The exhaustion of coal we destroy so wastefully might not be an irremediable disaster, for there are other sources of heat and power; but the metal famine that would follow a return to the metal supplies of 1800, or even 1850, would destroy the whole fabric of our civilisation.

The supply of metals can be maintained in two ways. We may work superficial alluvial deposits with more refined methods of metal recovery; or we may mine the more deeply buried primary ore-deposits.

The simple method of collecting ores is to wash the gravels that contain them in a tin dish; but this method is only profitable with ground so rich that it can be handled in small quantities. Poorer material can be washed in simple machines, but they are only successfully economically when the ore has undergone preliminary concentration by nature. Sluicing and dredging recover profitably the minute grains of ore scattered through thick sheets of barren material. Dredges work with marvellous economy. A dredge will haul up a ton of gravel from a river bed, sort it, wash it, and extract its gold, at the cost of three halfpence. It has been predicted that this invention, which we owe to New Zealand, will so greatly increase the gold yield of the world, as to repeat the revolutionary effect on prices occasioned by the gold discoveries of California and Australia in the middle of the last century.

But economical though these dredges be, it is doubtful whether they can maintain an adequate metal supply, and we are becoming increasingly dependent on the mining of deeper ore-deposits. They belong to two main groups:—

1. Ores of alluvial and sedimentary origin.
2. Ores deposited in lodes and masses.

Deep alluvial and sedimentary ores only pay to work for precious metals, and practically only for gold. They are of two main types: deep leads and buried sheets of gold-bearing conglomerates. The deep leads are the beds of

* A Discourse delivered at the Royal Institution, April 27, 1906.

old rivers, which have been buried under thick sheets of river deposits or lava flows. In working these deposits the course of the old rivers has to be discovered by boring through the overlying rocks; and when the old river system has been mapped out, the miner can pump the gravels dry, then dig them out, and extract from them their gold.

The only deeply buried, wide sheet of gold-bearing sedimentary rock which is of first-rate mining importance is the banket of the Transvaal. The banket is a marine conglomerate, composed of pebbles of quartz, and some pebbles of what is now pyrites. The rock was doubtless formed on a sinking shore-line. According to the explanation which seems to me most probable, the Rand gold was derived from the wearing away of gold bearing quartz lodes. The sheets of pebble-reef have been traced east and west through the length of the Rand; and they may occur to the south of Johannesburg, in the bottom of a great basin, far deeper than they can at present be profitably worked. Preparations are being made for mining the banket at the depth of 5000 and even 6000 feet, and if the gold be alluvial in origin, the limit of working will be determined by expense, and not by any limit in its distribution. It is, however, authoritatively held that the Rand gold is not alluvial in origin, but has been formed by impregnation, as in ordinary gold-quartz lodes. If so, the banket is only a very abnormal lode, and the downward limit of its ores will depend, not on the depth to which the conglomerate goes, but on the factors that control the deposition of ores in lodes.

Lode-caps.

The future metal supply of the world will doubtless come from ores deposited by secondary processes in lodes or masses, and the depth to which these ores extend depends on the depth at which these secondary processes can take place.

The lodes are generally first found and worked on the surface. The lodes may occur as walls of rock, left upstanding by the wearing away of the soft slates beside them. Lode mining began in Australia by a party of miners chipping out the pieces of quartz that contained visible gold from such an outcrop, and then breaking up the quartz with hammers.

The exposed part of the lode having been used up, the miners follow it downward as deeply as it pays them to go with the appliances available to them. Mining has shown that there are two main types of lodes; some ores are in flat sheets or veins, others in huge masses, which may consist of solid blocks of ore, or of rock impregnated by veins, veinlets, or even scattered grains. Both types of ore-deposits, when followed down, are often found to become thinner and perhaps to pinch out altogether. Even if the lode continue downward, there is soon a marked change in the character of the ores. Thus, in a gold-quartz lode, the work is easy near the surface, till the miner reaches the level where the rocks are charged with water; this change occurs at a depth which varies indefinitely, and may be as much as 1600 feet, but is often met at from 80 to 150 feet. Then comes a great increase in the difficulty of mining, and a great decrease in its profit.

Above water level the rocks are soft and decomposed, and full of cavities; below they are hard and compact; above that level they are dry, below they are wet, so water oozes into the excavations which have to be kept empty by costly pumping. The ore above water level is stained rust-red, and the gold is visible, so the good and barren ground are readily distinguished; below that level the ore is dark in colour, and usually charged with pyrites, with which the gold is combined, so it is no longer to be seen by the eye. The gold, moreover, may be associated with minerals, which may hamper its extraction. Hence, instead of the miner having to deal with an ore from which the gold can be easily obtained, it becomes refractory, and may require difficult metallurgical treatment. Again, the upper part of the lode being full of cavities, from which

heavy materials have been removed, a cubic foot of it weighs less than a cubic foot of the compact lode below, so the gold, if equally distributed, is richer per ton weight of ore above than below water level.

Hence a party of miners finds that a lode, which has paid them handsomely at first, in time becomes quite unprofitable; and the only thing to be done, when the incoming of the sulphides announces the end of the easily mined ore, is to sell the mine to a company, and start farming with the money.

The Lateral Secretion Theory.

The conversion of successful working miners into farmers was once stimulated by the widespread belief that these changes in the lodes indicated that gold is a surface formation, and that gold quartz lodes would not persist below the depth of about 300 feet. Thus, according to Sir Roderick Murchison, "as frequently as deep mines enriched the speculators who sought for copper and silver, so surely gold mining in the solid rock proved abortive, owing to the slender, downward dissemination of gold in a hard and intractable matrix." And he maintains that it is an "indisputable fact that the chief quantities of gold, including all the considerable lumps and pepitas, have been originally imbedded in the upper parts of the vein-stones." Murchison insisted repeatedly on the essentially superficial distribution of gold ores.

It is true that many of the earliest students of ore-deposits regarded all ores as derived from a "Pluto's Hoard" in the inner recesses of the earth. But this view was opposed to many of the most obvious facts. Thus lodes are often found to be closed below, in which case it is easier to explain them as filled from above, or from the sides, than from below. Again, lodes are often poor below and rich above, whereas the contrary would be expected if the heavy ores came from the interior of the earth. The veins known as gash-veins, which are entirely confined to one bed of rock, can therefore only have received their contents from it; yet the contents of these gash-veins are identical with those of the great fissure lodes, and so they also may have obtained their materials from the rocks beside them.

A further strong argument in favour of the local origin of the lodes is the character of the vein-stuffs, the non-metallic lode materials in which the metallic minerals occur. These vein-stuffs vary according to the rock beside the lode. Where a lode traverses sand-stone or other siliceous rocks, the vein-stuffs consist mainly of quartz; when it traverses limestone or igneous rock rich in lime, calcite is a common vein-stuff. In such cases it is obvious that the vein stuffs have been brought from the sides and not from below; and the ores are so intimately mixed with the vein-stuffs that it was natural to infer that both had been introduced by the same agency, and had been derived from a common source.

The lodes, moreover, in many mining fields show essential dependence on the rocks beside them, and apparent complete independence of the rocks below. Thus, in Cumberland, the lead lodes are apt to be broad and rich where they occur in limestone, and narrow and barren where they traverse shale and sandstone. Again, in the famous copper-field of Thuringia, the ores are confined to those parts of the veins that occur in a narrow band of slate, above and below which they are practically always barren. It was claimed that the ores had been originally precipitated from the water of the sea during the deposition of the copper-slates, and subsequently concentrated in the veins.

The first adequate scientific statement of the theory that the ores in lodes are leached out of the rocks in which the lodes occur, was by Bischof in 1847. His pupils endeavoured to justify this lateral secretion theory by demonstrating the existence of metals in ordinary rocks; but for thirty years their efforts were practically in vain. Then Fridolin Sandberger varied the method of search.

Most sedimentary rocks contain small quantities of

accessory minerals, consisting of fragments of the more durable constituents of igneous rocks. The bright idea occurred to Sandberger that if any metals occur in sedimentary rocks, they would be found in these accessory minerals. An element present as a mere accessory constituent, in a scarce accessory mineral, would form an infinitesimal proportion of the rock, and it would thus escape detection on a bulk analysis. So Sandberger first concentrated the accessory constituents, and then analysed these concentrates. The result was the discovery that minute quantities of various metals, including lead, zinc, copper, cobalt, nickel, &c., are widely distributed in rocks, and especially in the old slates, in which most ores occur.

This discovery removed the one objection to the lateral secretion theory that had appeared insuperable, for it showed that the common rocks, in which lodes occur, contain a supply of metal which lateral secretion can collect into lodes.

It is always a pleasure to solve a difficult problem by substituting known forces, working on accessible materials, for unknown agents, acting under conditions and on materials that must ever remain beyond the range of experiment and direct observation. So the lateral secretion theory at once sprang into popularity; and it was applied in one after another of the great mining fields of the world. Thus Emmons attributed the origin of the silver-lead ores of Leadville to lateral secretion from the overlying porphyrites. Becker derived the silver of the Comstock bonanzas from the adjacent diorites and andesites; Chamberlin and Kendal taught us to look for the source of the lead in the gash-veins of Wisconsin and of the North of England, to the limestone in which the veins occur; Howitt and Rickard advocated the view that the gold in the quartz lodes of Australia has been leached out of slates, into which it had been precipitated from the water of the Silurian seas.

But this fascinating and simple lateral secretion hypothesis is now generally abandoned. To mention only one strong objection, it does not explain the occurrence of lodes with different ores in the same country rock. Moreover, it supplies no explanation of the original source of the metals and the ores. For the metals found in the accessory minerals of sedimentary rocks are not necessarily present in them as primary constituents; they appear to have been subsequently introduced, for they are associated with minerals which the microscope proves to be secondary in origin.

The study of ores in recent years has made great progress by recognition of the fact that an ore is a rock, and must be studied on the same lines as ordinary rocks. The microscopic study of ores is throwing much the same light on their depth and distribution as it has done on the depth and genesis of igneous rocks. A rock is investigated both in the field and under the microscope in reference to three main problems:—first, the origin of the materials of which the rock is composed; second, the nature of the agents which have carried the materials to their present position; and third, what deposited them there.

The materials of any rock or ore can only come from one of three sources:—

1. Matter dissolved in the waters of the sea.
2. The igneous rocks which, either directly, or indirectly as the sedimentary rocks derived from their destruction, form the whole of the earth's crust.
3. The interior of the earth.

Sea-water as a Source of Gold.

Gold is the only metal for which the sea is considered a possible original source. The existence of gold in sea-water was first seriously advocated about fifty years ago to explain the occurrence of gold in some plates of Muntz metal that had been used as the sheathing of a ship, which had been trading for three years in the Pacific. It is true that plates of Muntz metal fresh from the works also contained a trace of gold. But the amount in the plates that had been exposed to the sea was larger than in new plates,

and the excess was explained as due to gold electrolytically deposited from sea-water. This view appeared the more plausible when, in 1872, Sonstadt announced that he had detected the presence of gold in minute quantities in the water of the Irish Sea. Professor Liversidge, of Sydney, who has followed up this question with greater perseverance than any other chemist of equal distinction, has detected from $\frac{1}{4}$ to $1\frac{1}{2}$ grains of gold to the ton of sea-water from samples collected on the coasts of Australia, and in the middle of the Indian and Pacific Oceans.

A grain of gold dissolved in a ton of sea-water is not a very large amount. One grain per ton is about 0·0000006 per cent. And condensed sea-salts, even if none of the gold were lost in evaporation, would have but 1 grain of gold in 78 lbs. of sea-salt, or one part in 546,000. To detect these amounts requires chemicals of wonderful purity and chemists of the highest skill. It is not, therefore, surprising that some chemists have failed to find gold in the sea, or have found it in far smaller quantities than Professor Liversidge has obtained.

But if gold be present in sea-water to the amount of only a grain to the ton, the gross amount is temptingly large, for it has been calculated that at that rate, there is enough gold in the sea to supply every human being with the useless dowry of 75 tons of gold.

Geologists accept the presence of gold in the sea on the authority of the chemists. But that the sea is the source of the gold in our lodes is a very different matter. The amount of gold in the sea is so small that it does not appear to follow the ordinary processes of precipitation. Gold is a metal that is very readily precipitated from solution. It is most likely present in the sea as some chloride, and gold is thrown out of chloride solutions by the action of light in the presence of organic matter. But some careful analyses of mud from the sea-floor, at positions where gold should be steadily precipitated by these agencies, have shown no trace of it.

Moreover, the essays of Dr. Don, confirmed by those of Mr. W. H. Bailey in the laboratory of the Mines Department of Victoria, have shown that the slates, from which the quartz lodes were supposed to have got their gold, contain none, except when they also contain pyrites; and the microscope proves that the pyrites was formed after the rock, and the gold was doubtless introduced simultaneously with the formation of the pyrites.

It is, in fact, far more probable that whatever gold the sea may contain was dissolved from the land, than that the gold on the land was derived by precipitation from the sea.

Igneous Rocks as a Source of Ores.

The igneous rocks are natural sources of iron and its allied metals, for iron is an essential constituent, often to a considerable extent, of the basic igneous rocks. Iron, moreover, is a material which, in the ample time available for ore formation, is easily rendered soluble by natural agencies. Hence the weathering of basic igneous rocks gives an ample supply of iron. It is removed in solution, and re-deposited in the films of rust, which colour red sandstones, and yellow sands and loams. Iron is the most widely diffused of all colouring matters; but rocks in which it may be conspicuous as a pigment may be of no use as an ore. A deposit is of no commercial value as an iron ore unless it contains at least 30, and usually from 50 to 60, per cent of iron. But the agencies that have leached out the iron from igneous rocks, and with it painted our landscapes, continue their action, and concentrate the iron as a serviceable ore.

Thus, the precipitation of iron carbonate by organic agencies in swamps, in lagoons, and along muddy shores, forms beds of clay ironstone, such as the black band ironstones associated with our coal measures, the marlstones of the Lias, and the ores which, in Roman and mediæval times, maintained the iron industry of the Weald.

Such ores are deposited contemporaneously with the rocks in which they occur; but other iron ores have been formed by the infiltration of iron salts into pre-existing

rocks. Thus have been formed the masses of valuable kidney iron ore in the limestones of the North of England. They have been formed where a bed of limestone is covered by a sheet of sandstone stained red by iron oxide. Rain-water, charged with carbonic acid from the air, or with organic acids derived from the decay of plants, percolates through the red sandstones, removes the iron as a soluble carbonate, and carries it down into the underlying limestone. Here the soluble iron salt is acted on by the limestone, some of which is removed in solution, and iron oxide precipitated in its place; and thus the masses of kidney ore are slowly formed, and grow at the expense of the surrounding limestone, as descending waters nourish them with fresh supplies of iron.

The distribution of such ores is limited by two factors. They are limited in area to localities where there was once an overlying, permeable, iron-stained bed to supply the iron; and they are limited in depth by the thickness of the limestone, and that to which water can descend through that rock, before the precipitation of all its iron.

The great deposits of hæmatite in the Lake Superior region, which have given the United States its supremacy in iron production, were, according to Van Hise, similarly formed by descending oxygenated solutions, carrying down iron from beds of iron carbonate. As the oxygenated waters necessary for this process cannot descend to any great depth, it is probable that the main mass of these ores will be limited to the depth of 1000 feet.

The beds of clay ironstone formed as contemporary deposits may, on the other hand, go down to great depths, when sunk in folds beneath thick beds of overlying sediments. The depth of such ores is a simple problem in stratigraphical geology, and the limit to which they can be worked is determined only by the cost of mining.

These iron ores derive their materials from igneous rocks indirectly; but there are some iron ores of direct igneous origin. They have been formed by the segregation of the metallic constituents of a molten magma into masses, or into bands along the cooling edges. The existence of such primary ores is indisputable; but their amount is still largely in doubt. They include masses of magnetite, and also ores of chromite, and according to some authorities, masses of copper pyrites, and of nickel-bearing pyrrhotite, and even cassiterite. There is no reason why these segregations should not form at any depth at which molten rocks consolidate; for both the pressure and heat would facilitate their formation, by allowing the molten work to cool so slowly that the segregation can collect the metallic constituents from a vast bulk of rock. Such igneous segregations usually occur in scattered patches; and it is only where they have been formed on the cooling margins of the rock that we have much clue to their distribution. But these ores are of secondary importance; because iron ores do not pay to mine at great depths; and it is only for iron ores that this igneous origin is conclusively established. There is no equal reason for regarding ores of such metals as copper, lead, zinc, gold, and silver as derived from igneous rocks.

The arguments for regarding igneous rocks as the source of ores in general, are their constant companionship and the frequent occurrence of traces of various metals in igneous rocks. Neither fact seems to me convincing. The frequent association of igneous rocks and ores is natural, for the intrusion of the igneous rocks supplies the heat, and makes the fractures necessary for ore formation. In regard to the second argument, it is true that minute traces of various metals have been detected in many igneous rocks, but usually in those of mining fields. It is very doubtful whether the metals are primary constituents. It is far more probable that they have been introduced after the consolidation of the rock, and at the time of the formation of the associated lodes.

The Barysphere as the Source of Ores.

For most ores we are therefore driven back to the third possible source—the hidden interior of the earth, which is

called the centrosphere from its position, and the barysphere on account of the weight of its constituents. This is an ample source of metals, for we may regard the earth as a vast ball of iron, hardened, like a modern projectile, by nickel, and no doubt charged with other metals. The rocks of the earth's crust are the stony slag given off from the cooling metallic mass. The one objection to this source is the great depth of the metallic barysphere; the specific gravity of the rocks at the surface is about 2.5, and that of the earth as a whole about 5.0. At the depth of 100 miles the specific gravity of the rocks is estimated to be about 2.8, or merely that of the basic igneous rocks. But in all probability the surface of the barysphere is not regular; projections from it rise into the lithosphere, and the mining fields probably lie over these projections.

There are areas, such as the Scotch Highlands, traversed by faults of colossal size; and with the rocks intensely metamorphosed and charged with quartz veins, but these veins are not to use the usual phrase, mineralised; there are enough quartz veins to maintain a large mining field; but, with insignificant exceptions, they are barren. The barysphere may be so far below that the quartz veins have not been charged with metals; whereas in other places, owing to the barysphere being nearer the surface, the veins received metallic, as well as non-metallic, minerals.

The Transporting Agents.

Accepting the barysphere as the source of metals, we have to consider the possible agencies by which they have been raised to their present level.

Iron has been brought to the surface of the earth by the intrusion of igneous rocks from the deeper parts of the lithosphere; and some quartz veins are also of igneous origin, having been formed as intrusions of molten rock. But these igneous quartz veins are barren, probably because they were too hot to be a suitable medium for the deposition of metals.

The great majority of ores have been formed by percolating water, as is shown by their arrangement in mass, by their microscopic structure, and by the minerals associated with them.

The introduction of ores in solution is indicated by what is known as "crustification"—their deposition in layers along the two walls of an ore-filled fissure; also by the frequent occurrence of geodes—cavities filled by the slow infiltration of material through cracks; also by the association of ores with such minerals as calcite, which are of aqueous origin, and the rarity of the typical minerals of igneous rocks, such as the feldspars and the pyroxenes; and when lodes contain minerals, such as quartz or mica, common to both igneous and sedimentary rocks, the varieties present are those deposited from solution or formed by the re-crystallisation of materials by crushing along fractures. Ores, of course, occur in igneous rocks; but in such cases they have usually been introduced in solution, and have replaced the original minerals.

The Descent of Meteoric Water.

The formation of most ores by water is now universally accepted, so their distribution in depth is controlled by the distribution of underground water. There are two sources of subterranean water. The first is the rain, which supplies the meteoric water. Some of this water runs off in rivers to the sea; another part of it, sometimes the whole, is restored to the air by evaporation, and the rest of it disappears by percolation underground.

The amount of this percolation seems to me to have been greatly exaggerated in the past. The amount lost by evaporation has been under-estimated, and the rocks have therefore been regarded as far more permeable than they really appear to be. This exaggerated estimate of the descent of the surface waters has been due in the main to three ideas.

1. An under-estimate of the amount of water available from other sources for the supply of deep wells. It was necessary to believe that a large percentage of the rain

must percolate underground, and that rocks are very permeable, so long as the deep artesian wells of arid regions were regarded as maintained by the rainfall on the distant hills, as when the flowing wells of lower Egypt were held to be nourished from the mountains of Darfur, and those of Central Australia by the rains on the distant Queensland Hills.

2. That water could descend by capillary action to great depths, even against high internal pressure, was maintained on the basis of an experiment by Daubrée. He inverted a vessel of water over a slab of porous rock, forming the roof of a cistern filled with high pressure steam. The water percolated downward in spite of the upward pressure of the steam; and hence it was claimed that capillarity could suck water downward against the resistance due to the earth's internal heat. But this experiment, as shown by Fisher and Kent, proves nothing, as the movement was toward a free air space, and there is no free air space in the earth corresponding to the cistern in Daubrée's experiment.

3. The third argument for the descent of the surface waters to great depths is based on the hydrodynamic principle, invoked by Van Hise, that a current of water will use the whole area of any channel open to it. If a stream of water be allowed to enter a deep trough, the current does not flow in a straight line from the point of inflow to the exit, but it slowly spreads downwards and upwards till the whole of the water in the trough takes part in the movement. Similarly, according to Van Hise, water percolating downwards at one place, and re-discharged elsewhere in springs or wells, is not confined to the direct line between the two places, but it spreads sideways through a great width of country, and sinks downwards to the greatest available depth. Hence, meteoric water should be universally diffused through a zone at a shallow depth below the surface. According to this conception the whole of one zone of the earth's crust is saturated by a great subterranean sea; and as its waters would be superheated, they would have great solvent powers, and being universally diffused, they would come in contact with all the metallic grains that may occur scattered through this zone of the earth's crust.

But the universal existence of this subterranean sea seems to be abundantly disproved by the evidence of many deep mines and wells. In Bendigo, *e.g.*, the ground water is confined to the surface zone, below which the rocks are dry, except where the levels happen to tap a spring of hot alkaline waters, which are probably of plutonic and not of meteoric origin. They are waters given off from the cooling magma of the earth, and belong to the same category as the fluids that, scattered in innumerable microscopic cavities, give quartz its milky whiteness and form the vast steam clouds, when, through a volcano, molten rocks reach the surface of the earth. These hot waters are therefore sometimes called magmatic on account of their origin from the rock magma of the interior, or juvenile, by Professor Suess, as they are making their first appearance on the earth's surface, or plutonic from their deep-seated origin.

This plutonic water answers all requirements for a depositor of ores. It is coming from the proximity of the metalliferous interior of the earth; it is superheated water—so it is a ready solvent of materials which are insoluble in a less heated water; and it is usually alkaline, and therefore is the readiest solvent of metallic sulphides—the primary condition of the vast majority of ores.

Changes in Plutonic Waters during their Ascent.

From whichever source the water comes, it is obvious that aqueously deposited ores must be limited to the depth at which water exists and works; and the range of ores of economic value depends upon the conditions which govern the precipitation of metals from underground solutions. Water, although its constituents may come from vast depths within the interior, is limited to a depth of perhaps only six or seven times the depth of existing mines.

The lower limit is due to the internal heat of the globe, which increases from the surface at a rate which may be taken as 1° F. for every 55 feet of descent. This is the traditionally accepted average; and the conditions are too uncertain to make it worth while at present to re-average it. Now water cannot exist at a temperature higher than its critical-point, 687° F. At the assumed rate of increase, that temperature would occur at an average depth of about 37,000 feet; the depth is probably much less in the neighbourhood of igneous rocks and in areas of recent volcanic action; and it may be much lower in ancient rocks in areas which have long remained geologically undisturbed, as, *e.g.*, in the Transvaal.

The figures that can be quoted are only rough approximations, and they will vary in different fields according to the conditions of increase of underground temperature.

At depths below about 37,000 feet, the temperature would be above the critical-point of water, which therefore could not exist as such. Its elements would be given forth as separate gases from the slowly cooling magma; the gases would rise, and having passed into a zone with a temperature below the critical, would combine to form water. This water would be at temperatures far above the normal boiling-point; but it would be kept liquid by the immense pressure of the overlying rocks. This water, owing to its tension, would tend to force its way to the cooler areas through any lines of passage open to it. They will be minute capillary passages, as nothing else could exist at such depths. Nearer the surface the pressure is less, so the spaces will gradually increase in size, and in them the water will collect and continue its upward flow. At length, it would reach a level, somewhere about the average depth of 18,000 to 20,000 feet, where the temperature would be about 400° F., at which water has its maximum capacity for solution; up to that level the water will be steadily dissolving materials, but above it the water will begin to deposit the material which it has brought with it from greater depths. The water has left the zone of accumulation, and has reached that of deposition.

According to the mode of deposition, there are three main types of ores:—

1. The steady ascent of the solution carries it continuously to regions of less and less pressure and of lower temperatures. Both changes favour deposition, and as the changes both in pressure and temperature are gradual, the material will be deposited continuously and fairly uniformly over a great vertical range.

2. A more rapid and patchy deposition occurs where the solution happens to come into contact with some rock, such as limestone, which decomposes the dissolved salts, and leads to the immediate precipitation of the metals, probably as sulphides.

3. When the solution approaches the surface, the rate of cooling is accelerated, and it may be mixed with surface waters, and thus the balance of the metals is quickly precipitated, and a high grade ore results owing to its deposition in a narrow range.

Hence most lodes have their richest ore bodies on the surface, for the agencies that lead to ore formation tend to rapid precipitation there, as the conditions are more complex and the variations in conditions more sudden.

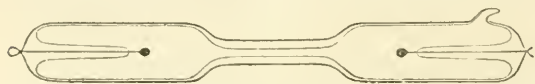
(To be continued).

Preparation of Adipinic Acid.—Erik Rosenlew.—The author prepares adipinic acid by mixing soda with a solution of cyclohexanone in water, and slowly adding a solution of potassium permanganate, meanwhile agitating with a turbine. The mixture is kept cold during the reaction by means of cold water. After decolorisation is complete the manganese dioxide is filtered off, the filtrate evaporated, and the adipinic acid set free by the addition of concentrated hydrochloric acid. The crystals thus separated out are re-crystallised once from hot water.—*Berichte*, xxxix., No. 10.

THE
PRODUCTION OF HELIUM FROM RADIUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

(MARCH 3rd, 1904).—A vacuum tube was made of lead glass of the shape and size shown in the drawing. The electrodes were platinum-wires, each inner end was curled into a loop, and on each loop a bead of radium bromide was fused. The tube was well exhausted, and a one-inch spark from an induction coil passed through. A considerable quantity of carbon dioxide was evolved at



first. This was pumped out, and the spark again passed, a condenser now being intercalated. More gas was evolved, and a sharp line spectrum temporarily made its appearance, but it was too faint for measurement. Carbon dioxide again was seen, and was removed by pumping.

The tube was well heated, exhaustion being continued; helium could not be detected at any pressure, but a sharp line made its appearance at about λ 569.

(JUNE 30th, 1904).—After about four months the tube was again examined with a one-inch spark.

Owing to the great dispersion, the light in the capillary tube was not strong enough to show the spectrum except by flashes, but there was no doubt as to the presence of a sharp yellow line. In order to separate helium and sodium lines a spectroscope was used that easily separated the yellow sodium lines, and fitted with measuring apparatus for getting wave-lengths. Sodium light was sent into the instrument from a spirit flame, and the index was set accurately on the sodium line, D_2 (λ 5890.2). The spark was then passed, and the yellow line of the capillary tube was seen to fall decidedly on the more refrangible side of D_2 , the distance separating them appearing to be about twice as much as that between the two sodium lines.

A stronger spark was employed, and now I was able to see the yellow line of the tube at the same time as the sodium lines of the spirit-flame. After some time the capillary tube became hot, and then sodium from the glass appeared, the three lines being visible simultaneously. Measurements were taken of the wave-lengths of the lines as follows:—

$$\begin{aligned} D_1 &= 5896.2 \\ D_2 &= 5890.2 \\ D_3 &= 5875.9 \text{ (helium)} \end{aligned}$$

The green line of par-helium was also seen, but it was too faint to measure.

The yellow neon line at 6266.7 could not be seen.

The radium was heated to redness with a spirit-flame, but it only had the effect of making the helium line a little brighter, and did not introduce any fresh lines. The line formerly seen at 569 could not be detected.

RADIUM.

LETTERS FROM "THE TIMES."†

(Continued from p. 127).

(August 18, 1906).

SIR,—The discussion which has taken place on the origin of the earth's heat leads one to question how far we are entitled to gauge the amount of heat set free by the disintegration of radium in the earth's crust.

Our laboratory experiments certainly show that radium in giving off heat, and the atomic alteration of the sub-

stance would be quite sufficient to account for it. I had 5 m.grms. of radium preparation, which was stated to be of 800,000° of activity, and it was quite possible to show that this, or rather the enclosure containing it, was perceptibly hotter than a similar enclosure containing an equal weight of any other kind of matter. But here we have the radium concentrated in a small bulk; it has a free surface, and therefore permits of the easy escape of particles, which by their mutual bombardment, or by the bombardment of surrounding surfaces, would give rise to the observed elevation of temperature.

Now, is it possible for the same freedom of action to occur when the radium is disseminated through enormous masses of rock?

One, of course, knows that the total radio-active effect depends upon the actual amount of radium, and not on the concentration; but, as there must be a hindrance to the free movement of the particles, it seems likely that inferences drawn from laboratory experiments may not be exactly applicable to the behaviour of radium imbedded in the earth's crust.

Is not the energy of the α -particle, and consequently its heating value, proportional to the freedom with which it can move, and is not this energy cut down very considerably by even a thin layer of air?

If a small quantity of radium were placed at the centre of a small lead sphere so that there was no space between the radium and the surrounding lead, would the latter show any rise in temperature?—Yours faithfully,

W. A. DOUGLAS RUDGE.

Woodbridge School, Suffolk, Aug. 15.

SIR,—The argument used to support the proposition that the salts of radium and the element itself disintegrate—namely, that it gives off helium—would be more satisfactory if helium did not already exist in the surrounding atmosphere. Is it not just possible that radium sorts it out from this atmosphere? And absorption of gases generally means rise of temperature. But of the mechanism of absorption and the sorting action accompanying it we practically know nothing, not even excepting the case of our familiar friend charcoal.—Your obedient servant,

JAMES C. RICHARDSON.

19, Claremont Square, Aug. 16.

(August 20, 1906).

SIR,—In your yesterday's issue I see letters of Sir Oliver Lodge and Mr. R. J. Strutt, replying to my letter to you of August 9 regarding radium.

After a kind personal reference to myself, Sir Oliver Lodge says, "But it is also known that" Lord Kelvin's mind "has not always submitted patiently to the task of assimilating the work of others by the process of reading, and our hope has been that before long he would find time and inclination to look into the evidence more fully." I am quite sure my old friend Lodge could not wilfully be unjust to me, but I do not think he knows how carefully and appreciatively I have done all I could by reading, and by personal intercourse with many of the chief workers in the field, to learn experimental results and theoretical deductions regarding radio-activity, ever since its discovery ten years ago by Henri Becquerel. I scarcely think any other person has spent more hours in reading the first and second editions of Rutherford's "Radio-activity" than I have.

Both Lodge and Strutt refer to the slowness of the extraction of helium from radium, in the process hitherto followed; and there seems to be good reason to believe that this slowness is essential. Strutt says, "If all helium has been removed from a sample of radium, it is found that, after an interval, a further supply can be extracted." The last clause shows that the initial "if" was wrong, and that some helium remained in the modified sample of radium. This view is thoroughly in accordance

* Abstracts from Laboratory Note-book.

† These Letters from *The Times* have reference to the Discussion on "Radio-activity and the Internal Structure of the Earth," at the York Meeting of the British Association (Section A), August 6, 1906.

with Rutherford's second edition (1905) p. 284, in which it is suggested that "uranium, thorium, and radium are in reality compounds of helium"; and, more particularly, that radium (atomic weight 225) may be a compound of four atoms of helium (atomic weight 4×5) and one atom of lead (atomic weight 205).

As to the suggestion, made first, I believe, by Sir George Darwin about three years ago, and favourably received by Rutherford, Strutt, and others, that our present underground heat, and sunlight, and sun-heat are due to radium, I must, for the present, limit myself to two sentences:—
1. Radium alone is quite insufficient, its duration as a source of energy being estimated by Rutherford (2nd edition, p. 458) as not more than a few thousand years, ("The average life of radium is 1800 years").
2. The suggestion that in uranium, thorium, actinium, and other matter capable of being "transformed slowly into radium," we have at least a million times as great a store of energy as we may think we have in radium, practically available for sun-heat and underground heat, is not validly supported by any experimental evidence hitherto published.—
I remain yours faithfully,

KELVIN.

Aix-les-Bains, Aug. 16.

(August 21, 1906).

SIR,—I am glad to have contributed towards eliciting Lord Kelvin's views on this subject. Those interested will no doubt judge for themselves whether or not the precautions adopted by Ramsay and Soddy, Himstedt and Meyer, and Curie were such as to make it certain that helium is continuously evolved from radium, as those writers supposed.

As to the internal heat of the earth, Lord Kelvin quotes the generally accepted conclusion that the life of radium is limited to a few thousand years. From this he argues that the radium now in existence has not been there long enough to heat the earth to its present high internal temperature. To this I reply that it is true that the actual radium now in existence has not done the work throughout, but that the supply of radium in the earth is maintained at a constant level by the production of fresh radium by uranium, contained in a small proportion in the rocks. Lord Kelvin, anticipating this reply, expresses his dissent from the view current among workers on radio-activity, that radium is continuously produced by uranium. I should like to ask a simple question. Lord Kelvin disbelieves that radium is being generated from any parent substance. How does he explain the existence of radium in the earth at present? On his own showing the identical radium now existing has not been there long. Is he prepared to assume that it was miraculously created in comparatively recent times?—I remain yours,

R. J. STRUTT.

40, Portman Square, W.

(August 22, 1906).

SIR,—Lord Kelvin's name is one which, during my officially "student" days and subsequent quarter of a century's college lecturing, I have taken not in vain but in earnest more frequently than that of any other physicist living or dead. Consequently, I trust that on the personal or biographical side general readers will take their cue from your leading article of last Saturday; but it would be wise for them to consider the scientific matters at present in debate as open questions to be settled by further investigation and discussion of laboratory facts, without undue insistence on weight of authority. I know that Lord Kelvin—from whom a further letter appears in your issue to-day—will be in accord with this recommendation, and I take the opportunity afforded by this little holiday correspondence to assure him of my profound and affectionate regard,—I am, Sir, faithfully yours,

OLIVER LODGE.

The Hermitage, Betchingley, Surrey, Aug. 20.

(August 24, 1906).

SIR,—In his letter published by you yesterday Mr. Strutt refers to experimenters who "supposed" that their work proved continuous evolution of helium from radium, and implies that I contest this conclusion. I never contested it. On the contrary, I feel that "supposed" is too weak a word. In fact, they found helium gradually beginning to show its presence in emanations from solutions of radium which at first showed no helium to the spectroscopic test.

Mr. Strutt, in his letter published yesterday, says, "Lord Kelvin expresses his dissent from the view current among workers on radio-activity that radium is continuously produced by uranium." This is an inadvertent misinterpretation of the last sentence of my letter in *The Times* of August 20, in which I only said that a particular suggestion going far beyond that view "is not validly supported by any experimental evidence hitherto published." We know nothing by experiment of the energy-value of the radio-activity found in igneous and in sedimentary rocks by Strutt and other trustworthy and able workers. The suggestions of Mr. Douglas Rudge on this subject in *The Times* of August 18 are important, and worthy of careful consideration.

Mr. Strutt asks me "a simple question"; how do I explain the existence "of radium in the earth at present"? My answer is—by concourse of atoms, and by interatomic motions, from a time when the ponderable matter of the solar system and the stars existed as separate atoms, scattered through the ether, and moving with velocities probably much less than the present velocities of stars through space. It seems to me fairly probable that the atoms of helium, and (?) lead, constituting the present radium, were, in later times, forcibly grouped together, among all the crystallisations which have constituted granite from a previously liquid earth.

I must apologise to you for trespassing on your space with mere guesses regarding prehistoric time. Coming down to the time of human history, I think we may agree with Mr. Douglas Rudge, and others who have suggested similar views, that a molecule of radium embedded in the earth's crust, under enormous pressures, probably has its constituent atoms safely protected against the explosive flyings asunder by which they produce the heating effects discovered in our laboratories.—I remain yours faithfully,

KELVIN.

Aix-les-Bains, Aug. 22.

(To be continued).

NOTICES OF BOOKS.

Researches on Cellulose. II. (1900-1905). By CROSS and BEVAN. London, New York, and Bombay: Longmans, Green, and Co. 1906.

THE period (1900-1905) covered by this book has seen the publication of much important work upon the constitution of cellulose, and the authors' review will be welcomed by all interested in the subject. The text is arranged excellently, and the appearance of the book marks a distinct advance in our knowledge of the nature of cellulose. The most important articles and papers on the subject which have appeared during these five years are either reprinted in full or else abstracted and then criticised by the authors, who, while they preserve a perfectly open mind upon disputed questions, and discuss the various views put forward without bias, are well qualified to be regarded as experts whose opinion is of the utmost value. The text is divided into three sections; the first gives a general *résumé* and forecast, discussing cellulose first as a typical colloid and then as a chemical individual, and finally considering some aspects of structural forms and dimensions of the celluloses. The second section gives an account of original investigations from 1900 to 1905, arranged as

explained above, and grouped as reactions of synthesis and reactions of resolution and decomposition, and the last part of the book is devoted to a short dissertation on technical progress in cellulose industries, and gives a very interesting summary of recent developments in this branch of technology.

A List of Official Chemical Appointments. Compiled by RICHARD B. PILCHER. London: The Institute of Chemistry. June, 1906.

This list of Chemical Appointments will serve a useful end if only as a guide for the increasing number of science students whose tastes would lead them to adopt chemistry as a profession, and who have not hitherto been able to obtain in a convenient form information as to the posts which might be open to them. Moreover, analytical and consulting chemists will find the publication of some value, and it will doubtless receive a cordial welcome in the scientific world. It contains lists of professional and teaching posts, and also appointments open to chemists in the various Departments of State in Great Britain and the British Colonies and Protectorates, together with, in many cases, summaries of the Acts under which the officials are appointed. For completeness sake some appointments are included which are not strictly chemical, but are connected with such subjects as agriculture, metallurgy, &c., and although every effort has been made to make the lists as comprehensive as possible, the compiler claims indulgence for errors or omissions, which will be granted readily as the book is the first of its kind, and is to be regarded as the forerunner of later and possibly fuller editions.

London Matriculation Directory, No. XLIII., June, 1906. London: University Tutorial Press.

THE guides to the Matriculation Examination of the University of London issued by the Tutorial Press are perhaps too well known to need recommendation. This volume contains the papers set in June, 1906, with comments upon them and full solutions, suggestions as to profitable courses of study, and the complete syllabus, both of matriculation and of some of the higher examinations of the University. The general hints and articles upon the choice of text-books contain some sound advice, and the book will be found invaluable, especially by private students who intend to enter for the examination.

Zeitschrift für Chemische Apparatenkunde. ("Journal of Chemical Apparatus"). Edited by PH. SCHUBERG. Berlin: Rudolf Mückenberger.

THIS journal, which was first published at the end of last year and appears twice a month, will be specially appreciated by two classes; in the first place, those who are engaged in research work will find that a study of its pages will repay them, for it will save them much time in their search for the best and most modern methods of solving mechanical problems; and secondly, directors of laboratories and chemical engineers will glean some useful hints from it. Thus, the discussion of the fitting up of some typical new laboratories is made a special feature, and the illustrations and descriptions of the new Institute of Technical Chemistry belonging to the High School at Berlin, for instance, are really valuable. Moreover, in reading periodical literature the chemist constantly comes across allusions to, or recommendations of the use of, various apparatus or materials with which possibly he is not familiar, and he will find it a great convenience to be able to look up information about them in this journal, which publishes useful articles upon such subjects as cryptol, the butyrometer, &c. While the original articles appear to come up to a high standard in every respect, the abstracts of papers in various periodicals dealing with mechanical appliances and contrivances are almost equally valuable,

and the new journal will no doubt continue to receive the support it well deserves.

Lists of Spectroscopes and Spectroscopic Accessories and of Echelon Diffraction Gratings. London: Adam Hilger, Ltd. 1906.

THE first of these two catalogues contains specifications of spectroscopes for general work and for special purposes; microspectroscopes and diffraction gratings, polarimeters, micrometers, and all kinds of accessories. The list is fully illustrated, and the latest improvements in the manufacture of spectroscopes are embodied in the instruments of this firm, which is well known throughout the world for the thoroughness of its workmanship. A price list of vacuum tubes and accessories is also included in the catalogue. List B contains details as to prices, &c., of the Michelson Echelon Diffraction Gratings, which the same firm has been manufacturing since 1899, and have now brought to a high state of excellence. The Auxiliary Constant Deviation Spectroscopes for use with Echelons are also described, special attention being called to the Hilger Wave-length Spectroscope, which presents some novelties in construction, and which has been found highly satisfactory in use.

Monumenta Pulveris Pyrii. By OSCAR GUTTMANN, M.Inst.C.E., F.I.C., F.C.S. London: The Artists' Press. 1906.

THIS beautifully bound collection of reproductions of ancient pictures concerning the history of gunpowder, of which only a very limited number of copies has been issued, is a work of both scientific and artistic value which is quite unique of its kind. The early history of a scientific industry cannot fail to be peculiarly interesting to present-day workers, and when it is illustrated by such a series of pictures, its value is increased in proportion to its vividness. The illustrations go back to the time of Roger Bacon, of whom there are two beautifully executed early portraits, and of Berthold Schwarz, whose labours according to the ancients were evidently directed by a horned and hooved adviser. All the first exceedingly primitive methods of refining saltpetre are depicted, as well as the preparation of charcoal and sulphur, the pictures of the early mechanical appliances being specially interesting. Among all the beauties of the illustrations it is difficult to pick out the best, but attention may be called to the frescoes in the former monastery of St. Leonardo in Lecetto, near Siena, which are excellently reproduced, and which contain representations of some of the earliest guns. The illustrations, as they began with Bacon and Schwarz, conclude with portraits of modern men of note, whose names have been made famous by their work on explosives. The explanatory text is written in three languages, English, French, and German, and the author has evidently thrown his whole heart into the production of this beautiful work of art.

Zeitschrift für Angewandte Mikroskopie. ("Journal of Applied Microscopy"). Edited by G. MARPMANN. Vol. XI. Leipzig: Hygienischer Verlag. 1906.

THE eleventh annual volume of this journal contains the monthly parts from April, 1905, to March of the present year. The chief feature of the publication is the prominence given to classified abstracts of papers dealing with clinical chemistry, the microscopical investigation of foods and feeding stuffs, technical products, micro-organisms, &c., which have appeared in other periodicals, and which are noticed in some cases at considerable length month by month. The majority of the original articles deal with subjects of biological interest; one very useful series consists of contributions to practical microscopy, and contains a good many practical hints and suggestions, while an article on radium and its action upon the eyes gives an interesting account of the results of experiments with radium bromide.

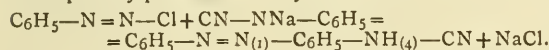
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 7, August 13, 1906.

Preparation of Pure Barium from its Sub-oxide.—M. Guntz.—When a mixture of magnesium powder and BaO are heated in an iron vessel enclosed in a porcelain tube to 1100° for an hour, the baryta changes its appearance and becomes blackened. This result is due to the formation of a sub-oxide, Ba₂O. When, however, a mixture of BaO and one-tenth its weight of Al is heated *in vacuo* to 1200°, a crystalline metal is obtained, containing 98.8 of Ba, which a second distillation *in vacuo* renders absolutely pure. This preparation of the metal is due to the intermediate formation of the sub-oxide Ba₂O, the dissociation of which produces the metal.

Aromatic Azocyanamides.—P. Pierron.—Though amides have no tendency to react on diazonium salts, the monatomic cyanamides do possess—probably by virtue of their more acid character—the property of forming compounds with diazonium salts. From these result, by their nitrogen substitution, a union with the benzenic or naphthalenic series. The author reacts upon the aromatic cyanamides with diazobenzol chloride. From the mixture thus obtained he extracts a yellowish red precipitate, which is the primary paramidoazoic cyanamide,—



By similar methods he prepares various other compounds.

A Property of Diastases.—J. Duclaux.—The name diastase is often used to denote two different things. Properly speaking, amongst diastases the majority (almost all) are colloids. The author has already shown that a colloid is composed of two parts, of which one—in bulk the larger—does not enter into any reaction, but simply serves to support the other (or active) part. After an exhaustive study of this latter portion, the author proves that it is essentially variable; it changes, not only by the action of salts, but by the simple addition of water, and the diastasic actions of metallic salts are attributed to this portion of the salt.

Copper Steels.—Pierre Breuil.—Already noticed.

MISCELLANEOUS.

The Chemical Laboratory at Wiesbaden.—During the Summer Term, 1906, the Chemical Laboratory Fresenius was attended by 41 students. Of these 30 were from Germany, 4 from England, 2 from Holland, 2 from Russia, 1 from Hungary, 1 from the United States of America, and one from Brazil. There were three assistants in the Instruction Laboratory, and twenty-seven in the Versuchsstationen (private laboratories). To the teaching staff of the Institution belong the Directors, Geh. Regierungsrat Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Prof. Dr. med. G. Frank, Dr. L. Grünhut, Dr. R. Fresenius, and J. Huber (Architect). The next Winter Term begins on October 15th. During the Summer Term, 1906, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen) on behalf of trade, manufacture, mining, agriculture, hygiene, justice, and government.

Session Commences Wednesday, Sept. 26.

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Experimental Physics	Prof. W. FRESENIUS, Ph.D.
Stoichiometry	L. GRÜNHUT, Ph.D.
Organic Chemistry	R. FRESENIUS, Ph.D.
Chemical Technology	Geh. Regierungsrat Prof. H. FRESENIUS, Ph.D. Prof. W. FRESENIUS, Ph.D., and Prof. E. HINTZ, Ph.D.
Microscopy, with exercises in Microscopic work	Prof. Dr. med. G. FRANK.
Chemistry and Analysis of Foods	J. HUBER.
Hygiene	
Practical exercises in Bacteriology	
Technical Drawing, with exercises	

The next Session commences on the 15th of October. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to one of the Directors.

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THE CHEMICAL NEWS.

Vol. XCIV., No. 2444.

NOTE ON OPALESCENCE IN FLUIDS NEAR THE CRITICAL TEMPERATURE.*

By SYDNEY YOUNG, D.Sc., F.R.S., Trinity College, Dublin.

THE phenomenon of opalescence at and near the critical temperature has been observed by Travers and Usher under exceptionally favourable conditions, owing to the great width (8 to 10 m.m. internal diameter) of the tubes they employed. The opalescence is, however, distinctly visible, and can be studied in much narrower tubes, such as those (0.15 m.m. internal diameter) used in my own investigations.

The experiments of Travers and Usher were carried out, for the most part, in such a manner that the total volume of the substance investigated remained constant, while the temperature rose very slowly. In my experiments, on the other hand, the substance was kept at its critical temperature,† and the volume was altered (usually diminished) by equal stages. The opalescence was always seen, but notes of its position and character were only made with a few substances—isopentane and normal pentane, hexane, and octane.

My observations—mostly unpublished—may be regarded as supplementing and, so far as a comparison is possible, confirming those of Travers and Usher, and the following generalisations may be deduced from them:—

1. When observations are made at the critical temperature (Cagniard-Latour temperature) at a series of diminishing volumes, no opalescence is visible so long as the volume exceeds a definite limit. When this limiting volume is passed, a slight opalescence appears at the bottom of the tube; that is to say, just over the mercury; at still smaller volumes the opalescence or mist becomes denser, and extends further up the tube. Near the critical volume the mist is very dense, especially near the middle: it may extend all through the tube, or the tube may appear clear either at the top or both at top and bottom. When the volume is further reduced, the mist disappears below, but becomes dense above, and on further compression the clear part extends upwards and the remaining mist at the top becomes less dense, and finally disappears at a definite volume.

When observations at the critical temperature are made at a series of increasing volumes, there is a tendency for the mist to be lower down in the tube than when they are made during compression. This tendency may probably be explained by the fact that each expansion causes a temporary slight fall below the critical temperature, and, consequently, a very slight condensation from the critical to the liquid state (in three cases it was noted that the meniscus was actually seen for a moment). Some little time would be required for equilibrium to be re-established after such a disturbance of the density, and it may be that the time actually allowed—one or two minutes at most—was insufficient. On the other hand, during each compression, there is a very slight rise of temperature, but this does not cause any change of state or disturbance of density.

2. When observations are made at a temperature slightly higher than the critical temperature, the mist is not only much less dense, but the range of volume over which it is visible is more restricted.

3. The limits of volume between which mist is visible at the critical temperature seem to be nearly the same for the

four paraffins examined (about 1.17 or 1.18 to about 0.87 or 0.88, taking the critical volume as unity in each case).

One conclusion drawn by Travers and Usher from their experiments is that "the opalescence is confined to that phase which is decreasing in volume through movement of the dividing surface, or, at least, is most intense in that phase." It happens, however, that in their experiments, whenever the liquid phase was small at first, it diminished, and when large at first it increased; and it may be doubted whether the above relation would be found to hold good for a phase which was large but decreasing in volume; for example, under the following conditions:—
(a) Constant volume and slowly falling temperature; (b) constant temperature and the total volume either large but decreasing, or small but increasing.

It seems probable from my experiments that the position of maximum opalescence really depends on the mean specific volume of the substance, being near the bottom when the volume is large, near the top when small, and near the middle at intermediate volumes.

This question, although it does not affect the main conclusions arrived at by Travers and Usher, seems to be of sufficient interest to repay further investigation.

A METHOD OF DETERMINING INDIGOTIN.*

By W. POPPLEWELL BLOXAM.

A CRITICAL examination of the various methods which have been proposed for the analysis of indigo was first undertaken.

The first consideration was the preparation of pure indigotin for use as a standard. Sublimation under diminished pressure proved to be the simplest method of obtaining pure indigotin. Indigotin was also obtained by re-crystallisation from nitrobenzene. Indigo "B.A.S.F. rein" was used as a starting-point for both these operations; by the former method 100 grms. can easily be prepared in a day, whereas the latter only gave a yield of some 30 grms. after a week's work.

The sulphonation of indigo and titration of the product with an oxidising or reducing agent is the basis of all practicable methods of analysis.

The oxidation with potassium permanganate of the sulphonation product of crude indigos gives only comparative results and not the true indigotin content of the samples, owing to the oxidation of the various impurities always associated with natural indigo. Two reagents have been suggested for the precipitation of these impurities; barium chloride by Rawson, and calcium carbonate (in excess) by Grossmann. Neither of these methods is satisfactory, for although some impurity is precipitated, there still remains in solution sufficient to upset the titration, and a still more important objection to both these methods is the fact that a certain amount of indigotin is always precipitated as the barium or calcium salt of the sulphonic acid. A closer investigation into these methods was made by preparing in a state of purity the mono-, di-, tri-, and tetrasulphonic acids, and studying the properties of their barium and calcium salts. The results confirmed the observations made above.

The reduction of the sulphonated indigo by titanium trichloride as proposed by Knecht was also open to objection, but by the application of various improvements in the experimental conditions this method proved to be very valuable for the titration of pure indigotin. It is little better than the permanganate, however, for titration with crude indigo; and if an indigo solution, of the concentration recommended for the reduction by Knecht, be purified by precipitation with an excess of chalk, so great is the loss of indigotin that pure indigotin gives a return of only 50 per cent.

* Abstract of a Paper read before the British Association (Section B) York Meeting, 1906.

* A Paper read before the Royal Society, June 21, 1906.

† In the case of normal pentane the "Cagniard-Latour temperature" and the "critical temperature" were found to be identical or at least indistinguishable (*Trans. Chem. Soc.*, 1897, vol. lxxi, p. 446).

In view of these results the idea of precipitating the impurities was abandoned.

Complete success was obtained, however, by precipitating the indigotin and leaving the impurities in solution. This was achieved by the use of potassium acetate. It was found that the quantitative separation of indigotin by this method depended upon the degree of sulphonation. This involved a complete investigation of the effect of different strengths of acid on indigotin for varying times and temperatures.

Sulphonation to the tetrasulphonic acid condition is necessary for the precipitation of a crystalline product; hence the name the "Tetrasulphonate Process."

If 1 grm. of pure indigotin is sulphonated for twenty minutes at 98° C. with 20 per cent fuming sulphuric acid, the tetrasulphonic acid is obtained without loss of indigotin. To obtain the same result with a crude indigo sulphonation with 25 per cent acid for forty-five minutes is necessary. The analysis is carried out as follows:—

100 c.c. of the indigo solution (of 1/500 concentration) are precipitated with 100 c.c. of a solution of potassium acetate (containing 450 grms. of salt in 1 litre of solution). The whole is warmed until resolution is effected, when it is cooled in a stream of running water and then placed in a vessel containing ice and water, and left for one hour. The crystalline potassium indigotintetrasulphonate is filtered off on the pump by means of a Gooch crucible with a well-fitting disc of filter-paper, and washed with an isotonic solution of potassium acetate.

The salt is then dissolved in 200 c.c. of water, and titrated under the improved conditions with potassium permanganate or titanium trichloride. To establish the method it was necessary to isolate the impurities of indigo; this was done by extraction, first with dilute acid and then with pyridine; both the products recovered from these extractions remained in solution after sulphonation and addition of potassium acetate. The accuracy of the process was finally proved by analysing a mixture containing known amounts of pure indigotin and these impurities; such analysis gave the theoretical amount of indigotin. The constitution and properties of the brown impurities extracted with pyridine are now under consideration.

A complete analysis was made of the Pemberandah Factory "Cake" for the season 1903-1904, and the results were calculated back to show the percentage of indigotin obtained from the whole plant. The figures reveal the fact that the efficiency of the present method of indigo manufacture is about 25 per cent of the total indigotin obtainable.* The attention of the Government of India will be called to this wasteful method of manufacture with a view to the introduction of the long-needed improvements without delay.

Clothworkers' Research Laboratory,
University of Leeds.

PRELIMINARY EXPERIMENTS WITH A CYANAMIDE COMPOUND AS A NITROGENOUS FERTILISER.*

By FRANK T. SHUTT, M.A., F.I.C.,
and
H. W. CHARLTON, B.A.Sc.

Of the elements of plant food necessary to return to the soil in order that fertility may be maintained, nitrogen is the most important, for not only is it the most readily dissipated by culture and cropping, but it is the most expensive to purchase in forms suitable for plant nutrition. It is evident therefore that any method which seeks to entrap the unlimited supply of free atmospheric nitrogen and convert it into a nitrogenous fertiliser would be one of great interest to the agricultural world. This will be the more apparent when we remember that "intensive" farming is becoming the order of the day, and that such calls for large amounts of available nitrogen. Further, if it is true that the beds of Chili saltpetre (nitrate of soda, one of the principal sources of agricultural nitrogen) are fast becoming exhausted, an economical process for the manufacture of a fertiliser from the air rich in nitrogen would open up an avenue for the profitable employment of capital.

The fixation of free nitrogen that we have here alluded to has been recently accomplished, though as yet no one of the several processes experimented with have, as far as we know, been sufficiently perfected to make it a commercial success. The source of energy employed to bring about the fixation is electricity, and the product usually sought calcium cyanamide. In the investigation about to be described the calcium and potassium salts of cyanamido-carboxylic acid were used. A sufficiency of these compounds for our preliminary work was kindly furnished by Mr. T. L. Willson and Mr. M. Haff, of the Willson Research Laboratory, Ottawa. The preparation of the compounds is described by Mr. Haff as follows:—

"A mixture of lime and carbon, through which a stream of air is passed, is brought to high temperature in the electric furnace by a suitable current. The mass, when perfectly cold, is lixiviated with cold water, filtered, and the filtrate evaporated *in vacuo*. When the solution is moderately concentrated it is filtered, carbonic acid gas is bubbled through, and the calcium cyanamide is precipitated as a calcium salt of cyanamidocarboxylic acid, $\text{Ca}(\text{CN}.\text{NH})_2\text{CO}_2$.

"To obtain the potash salt, the solution containing diluted calcium cyanamide is treated in the cold with dilute potassium carbonate, filtered, and evaporated *in vacuo* till a concentrated solution is obtained, keeping it warm and bubbling through it carbonic acid. The potash salt $(\text{K}.\text{CN}.\text{NH}.\text{CO}_2)$ is precipitated in needle-like crystals. The object in using the potash compound is to obtain a fertiliser that will furnish potash as well as nitrogen, and thus double its value as a fertiliser."

The experiments about to be described fell into two series. The first was to ascertain the effect of these compounds on the germination or vitality of certain seeds; the second was to determine the rate at which these compounds were nitrified or rendered available when present in the soil in various proportions.

Effect on the Vitality of Seeds.

It had been observed by investigators in Germany that cyanamide, if applied when the seeds were sown or only shortly before, had a decidedly poisonous effect, retarding germination and in some cases causing the death of the young plants. To verify this and to ascertain if some seeds had a greater resisting power to the action of the cyanamide than others, the following research was made:—The seeds chosen were wheat and peas, representing

Oxidation of Diphenyldiselenide, $(\text{C}_6\text{H}_5)_2\text{Se}_2$.—M. Stöcker and F. Krafft.—When diphenyldiselenide is treated with nitric acid, the seleninic acid is formed, and with chlorine water the seleno acid. The former is obtained as crystalline needles which explode on heating. From it the silver salt, $\text{C}_6\text{H}_5\text{SeO}_2\text{Ag}$, and the barium salt, $(\text{C}_6\text{H}_5\text{SeO}_2)_2\text{Ba}$, can be prepared. A well defined hydrate of phenyl selenous acid, $\text{C}_6\text{H}_5\text{SeO}_2\text{H} + \text{H}_2\text{O}$, or $\text{Se}^{\text{IV}}\text{C}_6\text{H}_5(\text{OH})_3$, is obtained when the silver salt is decomposed with hydrochloric acid. The silver salt of phenyl seleno acid is obtained by suspending phenyldiselenide in much water, heating to 50°, passing in chlorine, and adding silver oxide; from it the barium salt and the free acid (phenyl seleno acid) can be prepared.—*Berichte*, xxxix., No. 10.

* The percentage of indigotin contained in the whole plant (ordinary Indian varieties) being taken, as seems reasonable, at 0.6 per cent.

* *Transactions of the Royal Society of Canada, Second Series, 1905-1906, vol. xi., Section III.*

starchy and aluminous seeds, respectively. These were sown in porcelain basins containing each 4 pounds of soil. There were in all thirty basins, of which nine were checks and received no cyanamide compound. To secure uniformity of distribution the compounds experimented with were dissolved in water and then applied to the soils—the quantity varying as shown in the subjoined table. All the trials were kept under the same conditions as regards moisture, temperature, &c.

Effect of Cyanamide Compounds on the Germination of Seeds.

M.grms. of nitrogen added per 100 grms. of soil.	Results.
<i>Calcium Cyanamidocarboxylate.</i>	
0.5	Wheat and peas: Germination not retarded and plants not affected.
1.0	
1.8	
2.1	
3.7	
4.2	Wheat and peas: Germination retarded; plants slightly affected.
7.4	
10.4	Wheat and peas: Ditto, but injurious effects more pronounced.
14.9	Wheat plants badly affected. Peas, germination very much retarded.
20.9	
21.9	
<i>Potassium Cyanamidocarboxylate.</i>	
28.0	Wheat: Germination much retarded and plants soon withered. Peas, very few germinated.
29.3	
41.8	Wheat: Plants withered and died on reaching the height of a few inches. Peas, vitality of seed so far impaired that none germinated.
41.8	
1.1	Wheat and peas; Germination not retarded; plants unaffected and strong.
2.2	
4.5	
9.1	Wheat and peas: Germination retarded.
13.7	Wheat and peas: Germination retarded and wheat plants seriously affected.
18.3	Wheat and peas: Germination much retarded, especially in the case of peas. Plants of both very weak.

A consideration of the tabulated results will make it apparent that these compounds, save when present in very small quantities, injuriously affect the vitality of the seed. As the amount is increased the toxic effect becomes more and more noticeable, not only in the retardation of germination, but also upon the health and vigour of the young plants. Wheat is better able to resist this action than peas; nevertheless, the wheat plants in the tests containing the larger amounts of cyanamide frequently turned black, withered, and died after reaching a height of 3 to 5 inches.

A careful review of this work led us to conclude that the presence of the cyanamide compounds in amounts equivalent to 5 m.grms. or less of nitrogen per 100 grms. of soil would not prove injurious to the germination of seed. Toxic effects were markedly noticeable, however, with amounts between 10 and 20 m.grms. per 100 grms. soil, while still larger quantities proved fatal. The potassium compound appears to be more injurious in its action on the life of the seed and of the young plants than the calcium salt.

Trials were made with other seeds, but owing to an unfortunate accident the results were rendered useless.

Nitrification of the Cyanamide Compounds in the Soil.

The fact having been established that freshly applied cyanamide has a deleterious action upon the seed and young plants, it became a matter of considerable interest to learn what length of time is required to bring about in

the soil the conversion of the compounds under investigation into innocuous forms. And in this connection it may be remarked that even if these substances possessed no toxic action on vegetable life, their nitrogen would not be available for plant nutrition until they had undergone nitrification, since practically it is only as nitrates that ordinary farm crops obtain their nitrogen from the soil.

The experiments conducted to ascertain the rate of nitrification were carried on in plots holding five pounds of soil each. The soil throughout the series was uniform, and the estimations of the free ammonia and nitrates were made at stated intervals after the application of the cyanamide. Two pots were used as checks, and to these no cyanamide was added, but their ammonia and nitrates were determined on the same dates as those upon which the rest of the series were examined, so that changes normally taking place in the soil nitrogen could be followed. The methods used for the determination of the nitrogen compounds were those commonly employed in water analysis, and consequently the results may be considered as closely approximating the truth. Throughout the period of trial the soil in all the pots was kept under uniform conditions as regards moisture and warmth. The temperature of the room in which the pots were kept ranged from 65° F. to 75° F.

Experiment I.—This consisted of four pots each containing an amount of the calcium compound (37.84 per cent nitrogen) equivalent to an application of 22.5 lbs. per acre of a compound containing 16 per cent nitrogen. The experiment was begun on October 22nd, 1904, and estimations made on December 12th, 1904, and March 21st, 1905.

M.grm of nitrogen added per 100 grms. of soil	Nitrogen.		
	22/10/04.	12/12/04.	21/3/05.
As ammonia	0.36	—	—
As ammonia, nitrites and nitrates	—	0.042	1.442
As ammonia, nitrites and nitrates	—	0.787	0.088
As ammonia, nitrites and nitrates	—	0.829	1.530
As ammonia in check	0.026	0.017	0.249
As ammonia, nitrates and nitrites in check	0.275	0.682	1.231
Percentage of added nitrogen converted into ammonia, nitrites and nitrates	—	40.8	83.0

With small applications, as in this experiment, the conversion of the nitrogen of the cyanamide compound into ammonia proceeds fairly rapidly; the second and third stages by which the ammonium salts are converted into nitrites and nitrates are apparently of much longer duration. This would seem to indicate that the organisms instrumental in the production of nitrates and nitrites are susceptible to the toxic action of the compound.

Experiment II.—Was conducted upon a portion of the soils used in Experiment I., to which a further application of cyanamide was made, the amount being equivalent to 683 lbs. per acre of a compound containing 16 per cent nitrogen. The method of procedure was similar to that just described. The experiment was begun on March 21st, 1905, and subsequent determinations of the nitrogen compounds were made on March 28th, April 25th, and May 10th.

M.grms. of nitrogen added per 100 grms. of soil	Nitrogen.			
	21/3/05.	28/3/05.	25/4/05.	10/5/05.
As ammonia	1.442	—	—	—
As nitrates and nitrites	0.088	0.036	4.03	3.295
As ammonia, and nitrites and nitrates	1.530	3.904	5.387	4.941
As ammonia in check	0.249	0.394	0.299	0.133
As ammonia, nitrites and nitrates in check	1.231	1.045	1.950	1.650
Percentage of added nitrogen converted into ammonia, nitrites and nitrates	—	23.4	28.8	27.4

Experiment III.—In this series the potassium salt was used, the amount being equivalent to an application of 361 lbs. per acre of a compound containing 16 per cent nitrogen. The soil used, as in Experiment II., constituted a portion of that employed in Experiment I. The experiment was started March 21st, 1905, and subsequent determinations of the nitrogen compounds were made on March 28th, April 25th, and May 10th.

Nitrogen.

	21/3/05.	28/3/05.	25/4/05.	10/5/05.
M.grms. of nitrogen added per 100 grms. of soil ..	5.78	—	—	—
As ammonia	1.442	2.737	2.838	1.871
As nitrites and nitrates ..	0.088	0.058	0.416	1.281
As ammonia, and nitrites and nitrates	1.530	2.795	3.254	3.162
As ammonia in check	0.249	3.94	2.99	0.133
As ammonia, nitrites and nitrates in check	1.231	1.045	1.950	1.650
Percentage of added nitrogen converted into ammonia, nitrites and nitrates	—	25.1	17.4	20.0

The decrease in the percentage of nitrogen converted into available forms, as recorded in the last two tables, is apparent rather than real. It arises from the fact that there was a large and apparently unexplainable falling off in the available nitrogen in the check pots, the differences in which from time to time were necessarily used in the calculations to arrive at the conversion of the nitrogen of the cyanamide compound apart from that of the soil proper.

It would seem from a consideration of the data of this research that with the increase in the amount of the cyanamide compound there is a concomitant decrease in the rate of nitrification. This is probably due, as already indicated, to a toxic action upon the nitrifying organisms by the cyanamide compound, which action would naturally be increased the larger the application. On the other hand, it may in part be due to denitrifying changes leading to the loss of nitrogen in the free state.

The conversion of the nitrogen of the cyanamide into available forms is most probably, under favourable conditions, continuous, though not uniformly so. The first stage may be considered possibly as purely chemical, since water at ordinary temperatures converts the nitrogen of cyanamide into ammonia. The further changes being brought about through the agency of living organisms are necessarily slower, and will be regulated by many factors, prominent among which, as we have observed, is the proportion of the cyanamide compound present in the soil.

SULPHUR IN ITS RELATIONS TO OTHER ELEMENTS.

By JOHN CLARK THOMLINSON, B.Sc. (Dunelm).

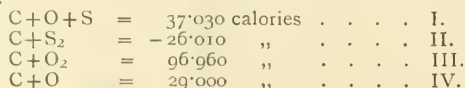
In carbon dioxide and disulphide we have two compounds to which, from their analogous relations to such compounds as urea, thiourea, &c., we assign a constitutional formula identical in each case.

The thermal behaviour of carbon, as shown in a previous article (CHEMICAL NEWS, vol. xciii., p. 37), warrants us

in assigning to it the formula $C \equiv O$, rather than $C \begin{smallmatrix} O \\ | \end{smallmatrix}$; therefore we are justified in regarding that of carbon disulphide as $C \equiv S$.

There exists an intermediate compound—carbonyl sulphide, COS—to those already mentioned, which, for the same reasons, we consider has a constitution represented by the formula $C \equiv O$.

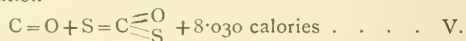
The following thermal equations represent the heats of formation of the above compounds, and of carbon monoxide, CO.



If we endeavour to determine the thermal value of sulphur in carbonyl sulphide as formed respectively from CO_2 and CO by the substitution and addition of an atom of sulphur, we can show that the results, as determined from two sets of data, are of the same magnitude; and that, applying the mean of these two results—for we are not justified in accepting either as being nearer the truth—to the heat of formation of carbon disulphide, we get an extremely close approximation between calculation and experiment, the difference being perhaps not greater than experimental error.

In the first case, we will suppose one carbon atom uniting with one oxygen atom and one sulphur atom as behaving thermally exactly as in the case of carbon dioxide, and that an oxygen atom is thermally equivalent in carbonyl sulphide and dioxide; then, from the thermal equivalents we have already shown are probable for carbon and oxygen (*vide* former article), $C = -8.130$ calories and $O = 52.545$ calories. Then the two atoms in uniting would cause a heat evolution = 44.415 calories, and as the heat of formation of carbonyl sulphide, COS, equals 37.030 calories, the difference between these two numbers will give the thermal value of the sulphur atom as -7.385 cal.

In the reaction in which carbonyl sulphide is formed from carbon monoxide and sulphur we have the thermal equation—



The carbon atom, in changing from the di- to quadrivalent form, causes an evolution of heat = 19.480 calories (Equations III. and IV.), and the difference between this number and that of the formation of carbonyl sulphide from carbon monoxide and sulphur (Equation V.) is $19.480 - 8.030 = 11.450$ calories, which, with the negative sign, or -11.450 , represents the absorption of heat due to the union of the atom of sulphur.

The mean of these two numbers, -7.385 calories and -11.450 calories, for the heat of combination of sulphur is -9.418 calories; and applying this value to our original formula for carbon disulphide, which we regard as having the constitutional formula $C \equiv S$, we find the heat of formation of this compound to be, by calculation, -26.966 calories, and that determined by experiment is -26.010 calories.

In sulphur dioxide, SO_2 , sulphur is more probably quadrivalent, $S \equiv O$, than divalent, $S \begin{smallmatrix} O \\ | \end{smallmatrix}$, the former being

the more stable form of combination; if $S \begin{smallmatrix} O \\ | \end{smallmatrix}$ were correct, we should expect—from analogy with hydrogen peroxide (H_2O_2) and water (H_2O)—ozone (O_3) and oxygen (O_2) to have a compound of the formula SO , and such has not been perceived.

The heat of formation of sulphur dioxide is 77.280 calories, and, from the thermal value of the oxygen atom ($O = 52.545$), we find the heat of combination of quadrivalent sulphur to be $-105.090 + 77.280 = -27.810$ cal.

For reasons similar to those in the case of sulphur dioxide, we should regard sulphur as hexavalent in sulphur trioxide, and, if so, the value -27.810 calories for quadrivalent sulphur should be the mean of that of hexavalent and divalent sulphur, and as quadrivalent sulphur has a thermal value -18.392 cal. greater than when divalent, the heat of combination of hexavalent sulphur should be $-27.810 - 18.392 = -46.202$ cal., which gives the heat

of formation of sulphur trioxide (SO_3) as 111,433 cals., and the value found by experiment is 103,320 cals. For sulphuric acid, which we regard as having the formula $\text{H}-\text{O}-\text{S}(\text{O})_2-\text{O}-\text{H}$, calculation gives a heat of formation 178,918 cals., and experiment 192,920 cals.; and for the acid of the formula $\text{H}_2\text{S}_2\text{O}_7$ the values are respectively 290,351 and 230,500 cals.

The above attempt at showing what is probably the thermal value of sulphur in some of its compounds helps us to see a distinct dynamical signification in the idea of valency.

RADIUM.

LETTERS FROM "THE TIMES."*

(Continued from p. 145).

(August 28, 1906).

SIR,—Your leading article (August 18) and recent correspondence show that an emphatic statement is needed to make clear to your lay readers:—

1. That radium is not an ordinary chemical compound.
2. That it does disintegrate with explosive violence.
3. That it is present in sufficient quantity to account for the heat of the earth.
4. That its disintegration is not altered by any known physical conditions.

Some experimental results obtained by me last spring at Montreal, under the guidance of Prof. Rutherford, are in good agreement with those found independently and by a different method by the Hon. R. J. Strutt. The equivalent amount of radium present in the upper layers of the earth was determined by the penetrating radiation resulting from the active matter. An account of this work has been communicated to the *Philosophical Magazine* and is in the printer's hands.

It is certain that radium does occur in sufficient quantity, and that its heat energy is of sufficient magnitude, to account for the existing temperature-gradients of the earth. Until we can conduct experiments in the interior of the earth, the radium theory is entitled to at least as much weight as the gravitation theory.

The recent discussion in your columns has resulted in a goodly crop of errors, written by those who have contented themselves with reading rather than with research work. I believe that no actual worker at the subject dissents from the general conclusions contained in Rutherford's "Radio-activity."

For example, it has been implied that radium is merely an ordinary compound of lead (?) and helium. But no ordinary chemical compound projects a particle, having the mass of a helium atom, with a velocity almost of the order of the velocity of light.

It has been stated that the disintegration of radium occurs too slowly to be detected by direct observation, and that is true. But some of the other active bodies, such as the subsequent products of radium, disintegrate with no less violence in a few minutes. It has been suggested that the disintegration may be retarded by pressure or by lack of concentration; but all the evidence—and there is much—indicates that the process of disintegration can neither be accelerated nor retarded by temperature, pressure, concentration, or other physical changes.

It is to be hoped that reverence for a great name and an honoured veteran will not induce your readers to regard lightly the brilliant and remarkable series of recent scientific discoveries in radio-activity.—Yours faithfully,

A. S. EVE.

Hull, Aug. 25.

(August 31, 1906).

SIR,—The correspondence started by Lord Kelvin in your columns would be incomplete if some one did not draw attention to the points of agreement as well as the points of difference between the distinguished scientific leader and the active workers in the field of radio-activity.

Lord Kelvin accepts as a fact, and, as he himself says, has never contested, the production of helium from radium. For this reason your leading article of the 18th inst., in so far as it tended to throw doubt on the validity of this fact, is misleading. If it is true that the spectroscopic examination of gaseous mixtures requires practical training and experience, it is equally true, for the same reason, that anonymous criticism of results obtained by those methods is intolerable. No spectroscopist of standing has openly questioned the result. Some who doubted the results as initially put forward by Sir W. Ramsay and myself have been convinced in the best possible way, by trying the experiment for themselves. Although their results, as so far published, have been uniformly confirmatory, it is perhaps not out of place to remark that none of them have proved as much as the original experiments—namely, that the radium emanation produces helium. The confirmatory labours of the foreign investigators have been mainly directed towards excluding the possibility of helium being occluded by the radium salt, whereas our experiments showed that a gas that had been condensed by liquid air, and so freed from free helium, developed the helium spectrum after some days. It is, in my opinion, a mistake to suppose that these experiments of themselves offered any conclusive evidence of the character of the change, whether chemical or transmutational, by which the helium was produced from the radium emanation.

Lord Kelvin argues that because helium is being continually produced from radium it is wrong to conclude that all the helium has been removed in the first place. Helium is, however, not the only new substance which a solution of radium continuously generates. I am speaking of facts that must be familiar to every one who has kept under observation a solution of radium in an air-tight vessel. The radium emanation is continually produced by the radium solution. The term "radium emanation" may be unfortunate, but it is used by workers in radio-activity to mean one definite product of radium of peculiarly definite material nature. It is a gas; it is condensed sharply at a certain temperature to the non-gaseous state; it has intense radio-activity of a characteristic kind; it generates in time a non-volatile radio-active product of new and equally characteristic properties; and last, but not least, it has been shown by experimental measurements to generate spontaneously in every second of time as much heat as the same volume of a mixture of hydrogen and oxygen when exploded to form water.

Now, if all the radium emanation is pumped off from a solution of radium, it is found after an interval that a further supply can again be extracted. Does Lord Kelvin argue that the "if" is wrong in this case also? The removal of the intensely radio-active emanation causes the β -radiation of the radium to become zero, and the α -radiation and the heat evolved both to fall to 25 per cent of the initial value, while the emanation and its non-volatile products emit the whole of the radiation and the heat which the radium has lost the power of emitting. With lapse of time the radium, kept in a closed vessel, regains its original activity, and then a new amount of emanation may again be pumped off and the activity of the radium again reduced as before. These processes have been carried out with a sample of radium in my possession for many years, yet it gives appreciably no less emanation now than formerly. If all the emanation that has been produced and extracted during these years was present in the original radium, why was it not at first incomparably more radio-active than it is now? We think therefore that there is ample justification for the conclusion that when no more emanation can be extracted from a radium solution it is for the reason that no more exists therein,

* These Letters from *The Times* have reference to the Discussion on "Radio-activity and the Internal Structure of the Earth," at the York Meeting of the British Association (Section A), August 6, 1906.

and that a real reproduction of the emanation with lapse of time is taking place. If this is true for the emanation it must be true also for the helium which is formed from the emanation, so Lord Kelvin's argument can be definitely answered.

It was upon evidence of this character, exhibited with wonderful uniformity by all radio-active matter, that the disintegration hypothesis was put forward by Prof. Rutherford and myself, long before helium had been thought of in this connection, and even before the magnetic deviability of the α -ray had been established. I must protest against the helium discovery being considered "isolated" or as being anything more than confirmatory.

I suppose that no one would wish to advocate the view that radium creates helium, the emanation, &c., which are known to be produced by it. In a sense, therefore, the products all pre-exist in the original radium, and the real question is as to the exact character of the decomposition by which they are formed. If chemists are antagonistic to the idea of atomic disintegration, they should be equally antagonistic to the idea, expressed in Lord Kelvin's letter of the 24th inst., of the formation of radium by the concurrence of atoms of helium and (?) lead, for radium has passed its chemical and spectroscopic examination for elementary character as well as the oldest elements known.

During a recent visit I had many long conversations with Lord Kelvin in which he honoured me with his views and criticisms on these topics. I found far less divergence of opinion between his views and those of active workers in the subject than I had imagined previously. The main differences seemed to centre round the propriety of using the terms atom and element in connection with substances which had been shown by experiment to undergo change. I do not wish to imply that the differences are merely of nomenclature. On the contrary, they affect the whole question which was discussed at York—at once the most important, the most interesting, and the most speculative in radio-activity at the present time—of how far conclusions drawn from the study of radio-active matter may be applied to ordinary inactive matter.

Of course my personal impression of Lord Kelvin's views may be quite mistaken, but I think I am safe in saying that he would not wish to be among those who seem in their antagonism to the "radium theory" to overlook the existence of radium as a fact. Lord Kelvin in his letters has indicated that he accepts the evidence that radium is continually generating helium and other bodies. This being so, I do not think that the remaining differences, although admittedly important, should divide him irreconcilably from us.

FREDERICK SODDY.

The University, Glasgow, Aug. 25.

(September 4, 1906).

SIR,—I am glad that Prof. Soddy has to-day summed up the amount of residual opposition in the radium controversy in a clear and forcible and yet conciliatory manner. Your columns did not seem to me a suitable medium for continuing a discussion which, judging from your leading article, struck outsiders as savouring of discourtesy to a veteran; but it is an eminently suitable vehicle for indicating a measured amount of agreement.

The key of the position is the elementary or the compound character of radium. Nearly all physicists, following Rutherford and Soddy in the first instance, now consider it to be a disintegrating element displaying a novel form of energy; Lord Kelvin and a few chemists enlisting under his banner pronounce it an explosively decomposing compound. All agree that it must be being "born" somehow, because of its comparatively short life; but whereas the experimenters assert that they know its parentage, Lord Kelvin thinks them too definite in that respect. There remains an outstanding difference with the Hon. R. J. Strutt about the source of the present heat in the crust of the earth; and that is about all.

The controversy about the elementary or the compound nature of the radium atom is not one that need be settled offhand. It does not really depend on the use of terms; there will be no need for chemists to alter the use of the convenient names "element" and "atom" because their etymology has become archaic, even when the physicists have turned out completely right. If radium splits up, as it does, it must in some sense be compound; and yet in every respect it behaves as much like an element, of the calcium-strontium-barium series, as any other element whose spectrum, atomic weight, and family relationship are known. Moreover, I believe that its instability, compared with that of other elements, is only a question of degree, not of kind; for radio-activity has been provisionally shown in the Cavendish Laboratory to be a property of nearly all matter.

Is it to be supposed that all the elements are compound then? That would not be at all a clear or helpful way of putting the matter. Chemical decomposition is affected by heat and by pressure; atomic disintegration is not likely to be affected by these external details; and radium has been shown by several workers to be appreciably unaffected by extreme heat or cold, and Schuster has found no influence of pressure up to thousands of atmospheres. In my judgment the burden of proof now rests with those who take the comparatively uninteresting view of the isolated nature of radium as a mere eccentric chemical compound.

Physicists generally are likely to feel, as I do, that, while expressing the greatest respect for the leader who as yet differs from them in some particulars, we must be fair to the workers in many parts of the world, to whom we owe this great extension of knowledge, confirmatory of the instability of the atom of matter already suspected by great mathematicians in accordance with high electrical and radiation theory.—I am, Sir, faithfully yours,

OLIVER LODGE.

The University, Birmingham, Aug. 31.

(To be continued).

ORE DEPOSITS AND THEIR DISTRIBUTION IN DEPTH.*

By Prof. JOHN W. GREGORY, D.Sc., F.R.S.

(Concluded from p. 143).

Surface Enrichment—Primary and Secondary.

THIS primary richness of the outcrop is reinforced by a secondary enrichment, to which the richest bonanzas and prizes of the mining industry are due. The secondary enrichment is, from a mining point of view, and especially in the valuation of a mining field, the more important process. Its nature may be illustrated by reference to a gold quartz vein, formed by an ascending solution, which had deposited gold uniformly in a vertical lode; if the ground containing the lode is slowly lowered by denudation, the gold in the uppermost part of the lode is dissolved by a solution formed by the action of surface waters on the iron pyrites in the lode. The gold is carried a stage lower, where the ferrous sulphate is reduced, and gold and pyrites re-deposited. So the cap of the lode now has concentrated within it the metals originally distributed through twice the length. The process is repeated again and again until a rich gold patch, such as the famous Londonderry pocket, may cap an otherwise worthless lode.

It is as an index of the extent to which ores have been thus secondarily enriched that the mineralogical study of lodes is of high economic importance.

All ore formation is essentially a process of concentration; the specific gravity of ordinary ores may be taken as 3.4; the rocks of the lithosphere have a specific gravity of 2.5; the barysphere must contain masses of a specific

* A Discourse delivered at the Royal Institution, April 27, 1906.

gravity of at least 6 and 7, and the average specific gravity of the average zone at the depth of 37,000 feet will be only 2.52. But as ore formation probably takes place where the barysphere is nearer the surface, its specific gravity at the critical temperature of water beneath a mining field in process of formation will probably be higher. But it can hardly be more than 3.0. So the metals in this zone of the crust will be more diffused than in a lode. The process of ore formation is the collection of the scattered particles, their concentration in a lode, and then the sorting out of the mixed, complex, primary constituents into purer, simpler, secondary minerals.

Thus, gold in a deep lode is always alloyed with silver, and probably with lead, zinc, and antimony as well. It is only near the surface that gold occurs with only 3 parts in the 1000 of silver; there are veins of native metals.

Similarly with silver; its deep ores are always alloyed with lead. It occurs as native silver and as horn-silver only in shallow ores.

Again, with copper, the primary ores are complex sulphides combined with iron. Thus the commonest primary ore is of copper chalcocopyrite with 34.5 per cent of copper and 30.5 per cent of iron; and the mineral occurs as streaks in iron pyrites, so that the copper is often only 1 or 2 per cent of the ore. This material is attacked, its constituents dissolved and re-deposited, probably as veins of bornite, which contains 55.5 per cent of copper and only 16.4 per cent of iron; and bornite often occurs in comparatively pure veins, the great bulk of the iron having been deposited apart as veins of hematite. The secondary bornite is then in turn attacked, and the copper re-deposited as the tertiary minerals, covellite, with 66.4 per cent of copper, or cuprite, with 88.8 per cent and no iron; and in the last stage in the process the copper occurs in veins or masses of native copper.

The depths to which ores will descend depend on the factors that control both their deposition and concentration. In considering the future of any mining field, the question of primary importance is whether the ores have been deposited by ascending or descending solutions, and we are beginning to acquire sufficient knowledge to form some idea as to the probable depths to which various types of ore-deposits will go.

Thus, there is no reason why gold quartz lodes should not go down to depths of about 18,000 feet below the level of the surface at the time of their formation. Hence, in estimating the depth to which any particular lode will go, we have to consider how much of the upper part of the lode may have been destroyed by denudation. In two adjacent mining fields, in one the lodes may continue to be auriferous to the depth of 5000 or 7000 feet from the present surface, whereas, in the other, where the lodes were formed in precisely the same way, the ore shoots may be quite shallow. The disappointing result in the second case is due to the upper part of the lodes having been removed by denudation, so that only the barren roots remain.

To plunge into deep mining regardless of the geological structure and history of the field is to invite failure. And deep mining to be profitable must be so organised as to work low grade ores economically, and to reduce dead work to a minimum by a plan of mining adapted to the geological structure of the field.

Gold mines worked thus at Bendigo have already reached the depth of 4250 feet, and the success there is the more remarkable as the mines are not working continuous lodes, but isolated masses of quartz. The reefs are saddle-shaped folds of quartz, floating in folded beds of slate and quartzite. It was not until the clue to the distribution of these isolated quartz masses was discovered that there was any chance of working the mines deeply. And though the field shows the usual decrease in grade, there is no indication that the lowest reefs have been approached.

In some fields the mines will be doubtless more shallow. Thus ores in lavas and horizontal stratified rocks, whether formed as contact deposits near igneous intrusions, or along fault planes and fractures, up to which hot solutions

have ascended, are likely to be patchy, owing to the sensitiveness with which such liquids respond to slight variations in the conditions. The depths of the ores will be directly determined by the thickness of the stratified rocks, and this is usually a simple problem of field geology. There is less probability of the ores continuing to as great a depth, as in infolded uptilted masses of ancient rocks.

The vast masses of pyritic ores represent a third type, which is of a special historic interest. They were at one time regarded, as they still are by some geologists, as bedded ores, precipitated in ancient lakes, by the action of decomposing organic matter, on materials introduced by streams. The ores were expected to continue to vast depths, because they are often hundreds of feet in width, and the horizontal extent of a sedimentary deposit is usually dozens, and may be hundreds, of times greater than its vertical thickness. So the depths of the ore-body was expected to be many times its thickness, and as one lenticular ore-deposit thinned out, others were expected to come in at slightly different levels. But these pyritic ore-masses have been found to be comparatively shallow in depth; none has yet been worked to the depth of 1000 feet, and for their shallowness there are excellent reasons; they are secondary deposits, formed by ore-bearing solutions replacing, particle by particle, shattered masses of rocks. The replacement has been so slow that the aspect of the original bedding is often still preserved, leading to the view that the pyrites itself was a bedded deposit. The shattered rock masses necessary for the formation of these huge ore-bodies can only occur near the surface; for at greater depths the weight of the overlying rocks would make the softer finer material flow into the interspaces between the harder fragments; the very force that fractured the rocks would also compress them, so as to render the crushed mass impermeable. Solutions might work their way along fractures, depositing ordinary fissure-veins, and replacement-veins on their edges; but there will be nothing like the widespread permeation which has produced the great pyritic ore-bodies. It is only natural that in these cases the mines should not reach the same depths as ores deposited along the channels of solutions escaping from plutonic depths.

Shallow and Deep Ore Types.

The distribution of ores in depth may therefore be usually inferred from a combined study of the geological structure of a mining field and the mineralogical characters of its ores. A definite conclusion is not always possible, as in the absence of these data, or when dealing with new types of ore-deposits. But in ordinary cases a general opinion can be expressed.

Thus there are three groups of ore-deposits which must be expected to have comparatively shallow limits. They are:—

1. Ores that have been deposited in fissures and open spaces, which cannot remain open at great depths. Hence, such ores if continued deeper, will be continued by ores of different character.
2. Ore-masses formed by the replacement of blocks of shattered rocks, because masses of crushed rocks at great depths would be closed by the flowing of the softer materials, and thus be impermeable to all ore-bearing solutions.
3. Ores formed by precipitation from descending solutions, including nuggets, bonanzas, and the various types of secondary enrichments, and also many ironstone masses and beds.

On the other hand, there are three types of ore-deposit which may persist to great depths. They are:—

1. Lodes characterised mineralogically by low-grade alloys, and complex sulphides with small percentages of the more valuable metals, and geologically by their occurrence as replacement veins along great fault planes, or as isolated bodies along lines of special permeability in folded rocks.

The limit in depth of such ores is the level of maximum saturation, which must occur, as a rule, at the depth of about 18,000 feet, for at that depth the ascending plutonic waters must begin to deposit their metallic salts.

2. A second group of ores with a possible great extension in depth are those of sedimentary origin, in tilted rock masses; for they can extend as deeply as such rocks can be buried without being metamorphosed by the earth's internal heat.

3. The third group of possibly deep seated ores are those formed by the segregation of metallic minerals from molten rock magmas.

These three groups of ores hold reserves of ore, the deep working of which is controlled by the elastic limits of expense. The assumed boundary of practical mining is being continually pushed downward. Once the final limit was accepted as 3000 feet, but there are already gold mines working at the depth of 4250 feet, and copper mines at 5000 feet, and preparations are being made for mining at 6000 feet. The greatest obstacle to deep mining is the high temperature; but that can be reduced by ventilation with compressed air or by the circulation of cold brine. It is unnecessary to suggest the powers given to the miner by liquid air. It gives him means of cooling and ventilation to which it is difficult to set a limit. There can be no doubt that the ore-deposits below the present limits of mining, for the existence of which the geologist can safely vouch, will one day be accessible. The profitable working of these deeper ores will require the close co-operation of the engineer and the geologist. Then the miner, armed with the invincible ingenuity of the engineer, and guided by the insight of the geologist, will follow the ore-shoots, in their irregular courses, into ever deeper layers of the earth's crust, and wrest from them their long hidden secrets and their well buried stores of wealth.

NOTES ON

AN ALLOTROPIC FORM OF ARSENIC

AND ON THE

ESTIMATION OF ARSENIC WHEN IN MINUTE QUANTITIES.*

By WILLIAM THOMSON, F.R.S.E., F.I.C.

I WISH to call attention to a peculiar allotropic form of arsenic which is produced when that substance is sublimed and rapidly condensed *in vacuo* or in presence of an inert gas, such as hydrogen or carbon dioxide. When in small quantities it condenses as a white film which rapidly becomes black. This blackening is brought about almost instantaneously by the light from a burning magnesium wire, or by bright daylight, but it takes place rather rapidly by ordinary gas-light, and the whiteness is not preserved when the film is kept in the dark. It continues white for a longer time when kept at the ordinary temperature of the atmosphere than when heated to, say, 100° C. It becomes black in about twenty minutes when cold and in the dark, and in about five minutes in diffused light.

A platinum-wire covered with a thin layer of glass upon which ordinary arsenic was laid was enclosed in a glass bulb. A vacuum was made in the bulb by a Töpler vacuum pump till no more air could be extracted, and left twenty-four hours over phosphoric anhydride. The pump was again worked, and proved that no leakage of air into the bulb had taken place. A current of electricity was then passed through the wire to heat it to redness, and so evaporate some of the arsenic, which condensed on the top of the bulb as a white film, and rapidly became black, as it did when sublimed in an atmosphere of hydrogen or of carbonic anhydride.

It occurred to me that this blackening action in the dark may be due to some obscure radiations which are everywhere present, and some experiments were made by enclosing these films in thick lead tubes, but they appeared to blacken when so enclosed just as rapidly as when enclosed in an ordinary wooden pencil case. Nevertheless, these white films may prove of interest to the physicist, as some means may be found for preserving their whiteness, and so making it possible to determine the presence of certain radiations as yet unknown.

On placing tubes containing these mirrors in liquid air they remained white for five hours, during which time they were immersed. The test mirror which was momentarily withdrawn from the liquid air from time to time became blackened, whilst the others which were immersed and in the dark, remained white.

I find that this form of arsenic has been studied by several observers (see Note), but more especially by Hugo Erdmann and Max von Unruh, who find that it is more volatile than the black form (which our observations confirm). They say—it is soluble in carbon disulphide, and whilst in solution it is not affected by light, but may be recovered as a yellow deposit on evaporation of the solvent, and it is then very sensitive to all kinds of light. On being left in solution in a stoppered bottle a reddish form of arsenic is produced which gradually falls from solution.

NOTE.—Schuller, *Math. u. Naturw. Ber. aus Ungarn.*, 1889, vol. vi., p. 94. Reigers, *Zeit. Anorg. Chem.*, vol. iv., pp. 403–409; vol. vi., pp. 397–320. McLeod, *CHEMICAL NEWS*, 1894, vol. lxx., p. 139. Linck, *Zeit. Kryst. Min.*, 1896, vol. xxvi., p. 280. Erdmann and Max von Unruh, *Zeit. Anorg. Chem.*, 1902, vol. xxxii., pp. 437–452.

Improvement in the Cooling Method for Condensing the Arsenic Mirrors in Arsenic Determinations.

The results obtained by the method which I formerly adopted of running a stream of cold water over a piece of tissue paper covering the drawn out portion of the tube, leave something to be desired, especially in the estimation of exceedingly minute quantities of arsenic, for the water at the edge of the paper next the flame does not give an exceedingly sharp line of cooling surface, and we have improved on this by taking a piece of block tin tube 8 inches long, having an internal bore of $\frac{3}{8}$ inch. This tube is flattened so that the internal measurements become $\frac{1}{2}$ inch $\times$ $\frac{1}{8}$ inch, and it is bent downwards in a curve about $\frac{1}{4}$ inch from the end. Two holes are made in the edges of the flattened tube opposite each other 2 inches from the bent end, and a thin silver-foil plate soldered over one of these holes. This plate is perforated by drilling in it a hole of a diameter sufficient to allow the drawn out portion of the largest sized glass tube to fit it. The tube is passed through the silver plate to the point at which the mirror is to be formed, and the water turned on through the tin tube, which is connected with the main by a thin rubber tube. A gentle flow of water is kept running through this tube, and it is found that if the length of the bent end of the tin tube is properly adjusted the water does not escape at the silver plate or the hole in the tin tube opposite, even when the tubes fit comparatively loosely. By this device 1/2000th of a grain per gallon of arsenic trioxide when working on 50 c.c. of the solution can be readily seen as a distinct narrow metallic ring, and the larger mirrors are more evenly deposited.

Influence of Nitrous Compounds on the Estimation of Minute Quantities of Arsenic.

I observed in making tests by the electrolytic as compared with the Marsh-Berzelius method that in some cases considerably larger mirrors were obtained by the latter than by the former, and on investigation it turned out that this difference was due to the fact that all the nitrous compounds used for the destruction of the organic matter had not been removed. To be certain of the results by the electrolytic

* A Paper read before the Manchester Literary and Philosophical Society, March 13, 1906. From *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, vol. l., Part III.

process it becomes necessary that the sulphuric acid should be evaporated to its fuming point, diluted with twice its volume of water, and again evaporated to the fuming point, and this should be again repeated to ensure the elimination of all of the nitrous compounds, so that the proper size and depth of arsenic mirrors may be obtained by the electrolytic process in the time allowed for the test. With the Marsh-Berzelius method the presence of some nitrous compounds does not so materially affect the result.

With a view of studying the influence of nitric acid in the electrolytic apparatus, a dilute solution equivalent to half a c.c. of the ordinary strong acid of commerce (0.48 gm. HNO_3) was added separately to an electrolytic apparatus—the first with a lead, the second with a zinc, and the third with a graphite cathode. This acid was gradually converted into ammonia in each apparatus, the amount of which was then determined. A current of 3 ampères was employed, and each apparatus was worked in series. After forty-five minutes the ammonia in the solutions in the various cathode chambers was determined, and the following results obtained:—

	HNO_3 reduced to NH_3 in 45 minutes.
Lead cathode (a)	0.22 gm.
Zinc cathode	0.21 „
Graphite cathode	0.10 „

(a) This lead cathode was made and kindly given to me by Mr. J. E. Hackford, of Nottingham. The lead used having been purified from traces of arsenic and antimony by him by fusing with sodium, and afterwards stirring up with pure fused sodium chloride while the lead is still at a high temperature.

This shows that the rate of decomposition was about the same with lead and zinc cathodes, whilst the graphite cathode only exerted about one-half the reducing action.

(To be continued.)

NOTICES OF BOOKS.

The Electrical Nature of Matter and Radio-activity. By HARRY C. JONES. London: Archibald Constable and Co., Ltd. 1906.

THE contents of this book were originally published in the form of a series of articles, which appeared in the *Electrical Review*, and which have been revised and consolidated into a single volume. The object of the book is to explain something of the theory of radio-activity from a non-mathematical point of view, and to expound the subject in such a way that it will be easily understood by the general reader, and will at the same time give him correct scientific views. While the treatment in many respects leaves little to be desired it is hardly interesting enough for a popular work, and extra attention paid to practical considerations would add to its attractiveness. Exception must be made in favour of an excellent chapter on theory, in which the facts which have been discovered are well discussed, and generalisations based upon them are skillfully deduced. Although the book makes no pretension to be regarded as a text-book providing a rigidly mathematical treatment of the subject, it will perhaps serve as an introduction to the study of a more advanced work.

Elementary Chemistry. Progressive Lessons in Experiment and Theory. Part II. By F. R. L. WILSON, M.A., and G. W. HEDLEY, M.A. Oxford: Clarendon Press. 1906.

THE second part of this course of experimental chemistry introduces subjects of a more strictly chemical nature than were contained in the first part, and the author's plan appears more satisfactory than when applied to the introductory physics and mensuration which were dealt with in the preceding volume. The preliminary sets of questions

which begin each chapter, and which the pupil is expected to answer from his general knowledge, ought undoubtedly to make him think, and give him some practice in reducing his thoughts to writing, which presents such difficulties to the average boy; while the teacher will be relieved of much supervision and explanation relating to details of manipulation, which are fully described in the directions for the experiments, the diagrammatic illustrations being very useful for the purpose. The attention paid to the historical aspects of elementary chemistry will awaken the pupil's interest, and help him to regard the science as one which is still living and growing, while the chapters on theory are also suggestive. Experience shows that a little theory is eagerly assimilated by those who have got to a certain stage of experimental knowledge, and the authors appear to have gauged very well the amount which is sufficient to awaken interest without making too great demands upon reasoning powers or faith; the simple electrical work introduced should also be valuable, and the course can be recommended for the use of pupils of about fourteen or fifteen years of age.

Forty-second Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. London: Eyre and Spottiswoode. 1906.

THE Chief Inspector's forty-second annual report on alkali and other works has to chronicle a revival of manufacturing activity in many directions during the year 1905, and a correspondingly larger number of visits of inspection and of tests. A *résumé* of the account of the investigations of the United Alkali Company with regard to the reactions in the Claus kiln is given, and recent important researches on subjects connected with the manufacture of sulphuric acid are also abstracted and discussed. A research on the analysis of ammoniacal gas liquors, with special reference to the distribution of the cyanogen compounds in them, and the conditions under which ammonium cyanide is a notable product, is communicated at length, and is of great interest for those engaged in processes for cyanide recovery, and a similar report on the conditions affecting the formation of ferrocyanides in sulphate of ammonia saturators is also included.

CORRESPONDENCE.

NEW CLASSIFICATION OF THE ELEMENTS.

To the Editor of the Chemical News.

SIR,—I have attempted a new classification of the so-called elements, a few series of which I give below. Instead of the usual method of adopting the atomic weight as the index to the behaviour of an element, I have taken the specific gravity as my guide. I have done so because the latter varies with the allotropic forms of the substance, whilst the former is looked upon as a constant. The specific gravity is therefore, in my opinion, a preferable index to the internal molecular state. P and S, among others, have a varying valency and also a varying specific gravity. Such variations give various affinities, which the atomic weight cannot indicate alone.

Os, 22.47	Ru, 12.26
Ir, 22.38	Rh, 12.1; Tl, 11.8
Pt, 21.5	Pd, Pb, Th, 11—11.4
Au, 19.3	Ag, 10.5
U, W, 18—19	Ta, 10.4; Bi, 9.8; Mo, 9
Hg, 14	Cu, Cd, 8.7
Ni, Co, Mn, 8—8.7	La, Cr, Va, 6
Fe, 7.9; In, 7.4	Ga, 5.96; As, 5.7
Sn, 7.3; Zn, 7.1	Ge, 5.5
Nb, Ce, 7	I, 4.9
Sb, 6.7	As, 4.7
Cr, Te, 6.26	Se, 4.3

The following compounds show the relationship which exists between elements classed differently by Mendeleeff:—
 K_2XO_4 , in which X may be either Ru, Os, Mn, Cr, Se, or S;
 XCl_2 , in which X may be either Hg, Cu, Cd, Te, or Se;
 $(XCl)_2$, in which X may be either Hg, Cu, or Se;
 K_2XCl_4 , in which X may be either Pt, Sn, or Zn.

The numerical relationships exhibited by elements grouped together are interesting, e.g.,—

The ratio of the at. wt. of Pt to that of Zn is as 3 is to 1.

"	"	Os	"	Te	"	3	"	2.
"	"	Cu	"	Te	"	1	"	2.

The atomic volume of Cu is one-half that of Hg; those of Zn, Pt are nearly equal, whilst that of Pb is just double.

The case of the atomic weight of Te is interesting, from the fact that it will not square with the Periodic Law of Mendeleeff. The same thing occurs with argon, which has the same numerical relationship with neon as Te has with Cu.

A relationship is observable in the fusing-points of some of the elements I have grouped together, e.g., that of S 387° absolute, Se 490° abs., and of Cd 593° abs. differ by a corresponding amount.

A similar arrangement of the oxides, the densities of which I obtained from Mendeleeff's admirable book, shows that compounds of an analogous composition fall into groups, just as the elements do. Does not this point to the "elements" being formed from still simpler bodies?—I am, &c.,

E. BRADBURY.

Bradbury's School,
16, John Dalton Street, Manchester, Sept. 10, 1906.

ALLEGED DISCOVERIES OF NEW METALS IN THE LAST CENTURY.

To the Editor of the Chemical News.

SIR,—On looking over some old newspapers in my collection, I found in one of them, *The British Luminary and Weekly Intelligence* for April 24, 1819, the following:—

"Dr. Vert, Professor of Chemistry at Gratz, has discovered in the Mine of Nickel, at Schladmig, in Styria, a metal differing from all those hitherto known. Its principal characters are—That it is not reducible except when combined with arsenic, its oxides are white, as are also the salts resulting from it. He proposes to give it the name of Vestium."

In the above extract, as will be seen subsequently, there are two mistakes—"Dr. Vert" should read "Dr. Vest," and "Schladmig" should be "Schladming."

Not knowing of any element in the present accepted list corresponding to the above in date of discovery, I searched the scientific journals of that period for further information, with the following results, which may interest your readers. In the *Philosophical Magazine* for 1819, p. 463, occurs the following passage:—

"*Vestium*.—This metal has its name from the discoverer, Prof. von Vest, of the Johanneum in Gratz. It is found in the nickel ore of Schladming (an ore mixed with cobalt pyrites) and also in cobalt ore. In its reguline state it has the appearance of iron, and has a fine granular structure. The existence of this metal is, however, questioned by Mr. Faraday and Dr. Wollaston."

Gratz is a University town and the capital of Styria, in which Schladming is a mining centre of some importance.

Dana, in his "Mineralogy," gives an analysis of cobaltine from Schladming, as follows:—

As	..	..	..	43.12	per cent
S	..	..	..	18.73	"
Co	..	..	..	29.20	"
Fe	..	..	..	5.30	"
Ni	..	..	..	3.20	"

99.55 "

In the same volume of the *Philosophical Magazine* (1819), on page 68, particulars occur of the alleged discovery of another new metal, in the following words:—

"*Woodianum*.—M. Lampadius gives the above name to a new metal which he has discovered in some English ores; but the characters of the ores are not mentioned in the letter he has addressed to Dr. Muller on the subject."

A later extract from the same volume (p. 305) reads:—

"*Woodianum*.—In our number for January we announced the discovery of this new metal by M. Lampadius. The material from which he obtained it was not English as first stated, but from Topschau in Hungary. It was considered an ore of cobalt, but was found to be composed of sulphur, iron, nickel, 20 per cent of this metal. Its colour is bronze-yellow, sp. gr. 11.47, it is malleable, has a hackley fracture, it is as hard as flint spar, it is strongly attracted by the magnet, does not tarnish at the common temperature, but does so when heated, forming a black oxide. It yields colourless solutions, but its oxide hydrated by ammonia is deep blue. Neither alkaline arseniates, nor phosphates, nor infusion of galls produce any precipitate in its solutions. Prussiate of potash gives a pearl-grey precipitate, and a plate of zinc a metallic one from its muriate solution."

Topschau is variously spelt Dodschau and Dobsina. Curiously enough, in the year following the appearance in the *Philosophical Magazine* of the above two extracts on woodianum, the following extract appeared in the *American Journal of Science and Arts*, p. 363 of the volume for 1820:—

"*A New Metal (Aurum Millium)*.—A letter from London to a gentleman in Baltimore announces the discovery of a new metal by Mr. Mills. The writer describes the 'Aurum Millium,' as it is called, as resembling gold in colour, very durable and malleable, and not expensive (the price being 4s. to 4s. 6d. per ounce). It is hard and sonorous, and has the valuable property of not easily tarnishing, and is nearly as heavy as jewellers' gold."

If the above paragraph stood by itself one would be inclined to think that the words "new metal" had been unscientifically and loosely used to describe a new alloy. Against this must be taken the fact that the journal was conducted by Benjamin Silliman, who was Professor of Chemistry at Yale College and correspondent for various learned societies, and it is unlikely that an editor of his standing would have permitted the words "a new metal" to be used in reference to an alloy. The similarity in the names of Mills and Muller mentioned in the above extract is, of course, apparent.

Further, the qualities attributed to the "new metal" appear to be almost exactly the same as those described as belonging to woodianum. The price quoted would be extremely low for a newly-discovered metal, but—on the supposition that the new metal is the woodianum above mentioned—this would be accounted for by the fact that it is stated to occur to the extent of 20 per cent in the nickel ore in which it was found.

It will probably be within the recollection of a large number of your readers that, in the year 1889, Professor G. Krüss (of Munich University) and F. W. Schmidt claimed to have discovered that both cobalt and nickel were composed of two separate metals (one metal being common to both), and they patented a process for the separation of nickel into the two metals. (Further particulars will be found in the *CHEMICAL NEWS* for 1889).

Dr. Fleitman, who claimed a very long experience in the nickel trade, contended that ordinary commercial nickel was composed of one metal only, and supported his argument by stating that, since Professor G. Krüss and F. W. Schmidt had announced their discovery, he himself had analysed a large number of samples of commercial nickel and had not been able to find the new metals described by Professor Krüss. There is nothing, however, that would

lead to the conclusion that he examined samples of the same material that Professor Krüss used.

We thus see that, between 1819 and 1889, at three different times, a new metal is alleged to have been discovered.

In the case of the so-called "vestium," so far as I can gather, there appears to have been no proof whatever that Professor Vest failed to uphold his claim. It is true that Faraday and Wollaston doubted the existence of the new metal, but this, of course, was only natural, but I cannot trace any analysis by them of the same ore as Professor Vest experimented with.

In the case of the alleged discovery by Professor Krüss, he probably claimed too much in asserting that ordinary commercial nickel was composed of two metals. The fact that nothing further seems to have been heard of his discovery may perhaps be accounted for on the assumption that he obtained his raw material from a smelting works, as in his patent specification he speaks of "nickel raw material obtained by concentration smelting." He may, perhaps, have experimented on samples of a parcel of ore, which, when he required further quantities for confirmation, had already been worked up in the smelting works. This might very well happen in a smelting works buying parcels of ore from different mines, and probably neither Professor Krüss nor the smelters themselves were able to identify the mine from which his original samples came.

With respect to the foregoing, it is worthy of note :—

1. That the alleged discoveries were made in two cases by competent chemists who were university professors, and whose opinion should be entitled to respect.

2. That in each case the alleged discovery of a new metal was made in a nickel and cobalt ore.

3. That these ores seem to have been found within a comparatively restricted area, viz., in Austria and Hungary, whilst nickel ores from Sudbury or New Caledonia apparently present no peculiarity.

4. That these alleged discoveries although not confirmed do not seem to have been disproved by any other observer experimenting with the same material.

5. That there is a remarkable similarity between some of the properties of Woodianum as described in 1820, and the metal which Professor Krüss claims to have discovered in 1889.

Woodianum.

Bronze-yellow in colour. It has a black oxide. Solutions colourless. Specific gravity, 11.47.

Prof. Krüss' Metal

When present in nickel to the extent of about 2 per cent communicates to it a yellowish shade. Has a black oxide. Solutions colourless. Admixture of 2 per cent with nickel appreciably increases the sp. gr. of the latter metal.

On the other hand, assuming that the two metals are identical, there is a serious discrepancy. Woodianum is described as being precipitated by metallic zinc; Professor Krüss distinctly states that his metal is not so precipitated, and bases his process of separation from nickel on this fact. Assuming, however, that Woodianum and Professor Krüss' metal are the same, several solutions of this contradiction occur to one, of which the most likely to my mind are :—

1. The possibilities of the metallic precipitate obtained on the zinc being some other metal than Woodianum, overlooked as being present by the discoverer of the latter metal.
2. The possibility of Professor Krüss' metal being precipitated on the zinc only after the last trace of nickel had been removed (see his patent specification) by the zinc. Assuming insufficient time had been given for the new metal to precipitate after deposition of all the nickel, Professor Krüss may have been misled on this point. He does not appear to have tried the effect of zinc on a solution of pure salt of his new metal.

Professor Krüss tried to obtain spectroscopic evidence of a new metal, but the result was apparently unsatisfactory. Unless the material were free from all trace of nickel, cobalt, and iron, metals whose spectra are very complex, it would be a very long and tedious investigation even for a skilled observer working with good apparatus.

Looking at the above facts and observing the number of coincidences, there is, I think, ample ground for further inquiry as to whether in the nickel and cobalt ores of Hungary and Austria :—

1. There are metals at present unknown to us; or,
2. Whether in these ores metals that are known exist in such combinations or admixture as to so modify their normal qualities as to lead skilled observers to think that other and unknown metals are present.

In the extracts given above the localities of Schlading and Töpschau are specifically mentioned. If any of your readers should have business or other connections with these localities, it should not be difficult for them to obtain samples of ore from the various parts of the old dump heaps of such nickel or cobalt mines in the neighbourhood as are known to have been working in 1819.

An analysis of these might lead to the re-discovery of "Vestium" and "Woodianum."—I am, &c.,

C. T. OWEN.

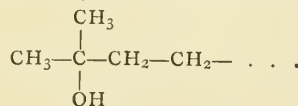
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CHEMICAL NOTICES FROM FOREIGN SOURCES.

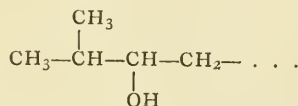
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 8, August 20, 1906.

Boiling-points of certain Secondary and Tertiary Alcohols.—G. D. Hinrichs.—Considering the formulæ of tertiary and secondary alcohols to be—



and—



respectively, the author calculates the mass of the molecule, and hence finds the moment of inertia. He finds that for tertiary alcohols the values of the moments of inertia are smaller at the beginning of the series, but increase rapidly when the chain is prolonged, and soon exceed those of the secondary alcohols; the boiling-point is a function of the maximum moment of inertia. Thus these temperatures should increase in the same proportion, and this result has been proved both empirically and directly.

Researches on the Relation between Functional Groups in Distant Positions. Decamethyleneimine.—E. E. Blaise and L. Houillon.—The authors find that the relations between functional groups in the same molecule are not a periodic function of the position of these functional groups, or, at least, nothing hitherto discovered proves such a relation. This conclusion seems to be general, and to apply equally to the closing of carbon chains containing one atom of oxygen. Further, if the compounds which M. Krafft obtains are well-defined bodies, and if the properties attributed to them are exact, the base which accompanies hexylpyrrolidine is different from decamethyleneimine; this latter being non-existent.

No. 9, August 27.

Copper Steels.—Pierre Breuil.—The author makes a detailed investigation of copper steels containing from 0 to 10 per cent of copper with regard to (1) the breaking by shock, (2) torsion, (3) hardness, (4) corrosion. In the latter case the loss by corrosion is considerably less than that of the same steels without copper. With regard to the nature of the constituents, these steels do not differ very much from ordinary steels, except that the form, distribution, and quantity of these constituents are such that the special properties indicated in the paper are of the same interest to metallurgists as steels containing nickel or other metals which have a higher price than copper.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 10, 1906.

Heavy Metal Salts of very Feeble Acids.—H. Ley and F. Werner.—By adding sodium hydroxide to a mixture of solutions of cobalt acetate and succinimide, a crystalline precipitate of cobalt succinimide, $\text{Co}(\text{NC}_4\text{H}_4\text{O}_2)_2 \cdot 6\text{H}_2\text{O}$, is obtained, and the analogous nickel and copper salts can be prepared similarly. When the last named salt is hydrolysed probably the normal hydroxide, $\text{Cu}(\text{OH})_2$, is first formed, and gives up water at the ordinary temperature, yielding a hydrated copper oxide, $3\text{CuO} \cdot \text{H}_2\text{O}$. If camphoric acid imide is used instead of succinimide a compound containing both alkali and copper is obtained; it may be regarded as the sodium salt of a complex copper camphoric acid imide. These salts (with the exception of the nickel salt) are typical examples of exceedingly easily hydrolysed salts, which in solution in presence of excess of the free feeble acid are quite stable, but are readily hydrolysed in pure aqueous solution in the cold. The nickel salt of succinimide is much more stable than the cobalt compound, and there are indications that on hydrolysis the nickel hydroxide appears in the form of the unstable hydrosol.

Decomposition of Hydroxylamine in presence of Hydrogen Ferrocyanide.—K. A. Hofmann and H. Arnold.—If equal weights of potassium ferrocyanide and hydroxylamine chlorhydrate are boiled in aqueous solution, ammonium chloride and nitroprusside salt result, while nitrogen and hydrocyanic acid escape and a blue crystalline powder is precipitated. This precipitate is a new substance which appears to be a ferriammonium salt of hydrogen ferrocyanide, and corresponds to the formula $\text{Fe}_2\text{C}_6\text{N}_6\text{NH}_4$. According to Hofmann, there are four ferri-potassium ferrocyanides of empirical formula, $\text{FeCy}_6\text{FeK} + \text{water}$, differing from one another, both physically and chemically, and the new ammonium compound is undoubtedly analogous to the one which has the structural formula $\text{K}(\text{FeCy}_6) : \text{Fe}_2^{+++} : (\text{FeCy}_6)\text{K}$. In behaviour and colour it agrees perfectly with Williamson's violet, and hence its structural formula is $\text{NH}_4(\text{FeCy}_6) : \text{Fe}_2^{+++} : (\text{FeCy}_6)\text{NH}_4$. No change occurs even when this compound is boiled for some time with 5 per cent potassium nitrite solution, and thus the ammonium group is very firmly bound. Iron chloride solution has no action on the substance.

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THE CHEMICAL NEWS.

VOL. XCIV., No. 2445.

THE APPLICATION OF PHOTOGRAPHY TO THE SOLUTION OF PROBLEMS IN CHEMISTRY.*

By WALTER NOEL HARTLEY, F.R.S.,
Royal College of Science, Dublin.

THERE can be no doubt that those rays in the spectrum of an element which cannot be readily recorded on a photographic plate are of little practical importance to the chemist; while, on the contrary, those which lie beyond the region of visibility are not only more numerous, but in general they constitute the most characteristic part of the spectrum of each element. An instrument which adds enormously to our powers of investigation is the spectrograph. In its simplest form it consists of a slit, two lenses, and a prism, all of quartz, in combination with a very accurately focussing camera. It records on a photographic plate the rays emitted by a substance, whether they are luminous or not, and it arranges them in the order of their refrangibilities from wave-length 4681 to 2025, with all intermediate lines sharply focussed. By the use of isochromatic plates the less refrangible rays in the red may be simultaneously photographed.

The many and various problems which the chemist is called upon to solve may be considered under two categories:—(1) Problems of composition, or analytical problems; (2) problems of molecular structure. I propose to give an account here of the applications of the spectrograph to chemical analysis, the practical applications to organic chemistry being dealt with in another section.

Problems connected with the Composition of the Atmosphere.

The spark spectra of the elements are individually composed of a great number of lines presenting different characteristics, both in length, intensity, and shape, and it may be readily understood that an element can be identified by what may be termed its portraiture. Out of 2050 lines occurring in the spectra of sixteen solid elements, not four can be found to occur in any two spectra.

Some lines which appear to be common to all the different spectra belong to the gaseous elements of the atmosphere, and their total number, as originally photographed, was 195. They were proved (in 1887) to be due chiefly to oxygen and nitrogen, by photographing the spark spectra of metals in gaseous compounds composed of those elements—as, for instance, in nitrous oxide. But the spark spectrum of air, as photographed, mapped, and described by Hartley and Adeney, contains various lines which could not be attributed to oxygen or to nitrogen nor to any other substance (*Phil. Trans.*, 1884, clxxv., 63). It had been observed that many of the atmospheric lines were subject to variations according to circumstances which were completely under experimental control, but that aluminium, indium, and copper electrodes yielded air spectra with some lines more sharply defined and distinct and more prominent than others (*Journ. Chem. Soc.*, 1882, xli., 84).

These facts were again studied in 1887 and 1890, but reserved for a more complete examination. In the year 1894 it was announced that Lord Rayleigh and Sir William Ramsay had separated a new element from the atmosphere. A proof of their paper, in advance of its publication, was forwarded to me from the Royal Society on January 29th, 1895; this contained a description of the spectrum of argon by Sir William Crookes. All the lines he had

measured of greater refrangibility than wave-length 4629·5 were found in Hartley and Adeney's photographed spectrum of air, published in 1884.

Fifty of these air lines, out of a total of 195, which had been proved not to belong to oxygen or nitrogen (*Proc. Roy. Soc.*, 1895, lviii., 193) were identified with argon lines. This fact, with the actual wave-lengths of the lines, was communicated to the Royal Society at the same meeting at which the papers describing the discovery of argon were read. A letter from the Secretary at that time, Lord Rayleigh, now President of the Royal Society, informed me that my communication had been recognised as independent evidence of the existence of argon in the atmosphere. Eighteen days later I pointed out that the conditions as to pressure of the argon, and the nature of the electrodes used in photographing the spectrum of air, were very nearly those under which the brightest and purest spectrum of argon had been obtained. The spectrum of argon, then, had undoubtedly been photographed, and many of the lines accurately measured, along with those of oxygen and nitrogen, for the first time in the laboratory of the Royal College of Science, Dublin, and published ten years before its existence was announced by its actual discoverers.

A most complete investigation of the argon spectrum was made by Professors Eder and Valenta, and published in Vienna in 1896. On the accompanying table are shown the wave-lengths and descriptions of the lines in question, compared with the corresponding measurements by Crookes and by Eder and Valenta. Eder and Valenta's were made with a Rowland concave grating of 30 inches focus, and those of Hartley and Adeney with a Rutherford plane grating of 17,296 lines to the inch and quartz lenses of 36 inches focus.

Without the aid of photography it would have been impossible to establish the fact that the spark spectrum of air contained fifty lines which did not belong to the spectra of any of its known constituents.

The fact that argon gave two different spectra was considered to be evidence to the effect that there were two substances in argon, and therefore it was a compound. Evidence to the contrary was—(1) that many substances have two different spectra, and that there had been photographed on the same plate, simultaneously from the same spark discharge, the two different spectra of nitrogen; (2) that there were no gaseous substances known which could withstand the high temperature of the condensed electric spark without exhibiting the spectrum of one or other of the elements of which it is composed. It was even argued that it was probably a modified form of nitrogen, even as ozone is a modification of oxygen. But as the spectrum of argon of either the blue or the red modification was not that of any known substance, it followed that if argon were a compound it must be a compound of a new element.

That which was described as the true distinction between a compound and an elementary substance, with special reference to argon, has been recognised as the criterion of an elementary form of matter by the International Congress for Pure Chemistry, which met in Paris in 1900.

The absorption properties of the constituent gases and vapours in the earth's atmosphere causes the limitation of the solar spectrum, and the late M. Cornu, of Paris, showed that this limitation diminishes regularly when photographs are taken at increased altitudes, up to 2570 metres above the sea-level. In 1881 each of the minute constituent substances known at that time to be present in the air was examined, and the absorption effect on the ultra-violet spectrum of small quantities of each of them was carefully determined. The one substance which in minute quantities was found to cause the greatest amount of absorption was ozone, and varying quantities above a certain limit caused the spectrum to be shortened almost exactly at the same point which was described as being the maximum absorption of ozone. This position coincided with the extreme end of the solar spectrum. The conclusion arrived at was—that neither dust in the atmosphere, nor the vapour of

* A Paper read at the Sixth International Congress of Applied Chemistry, Rome, April 28th, 1906.

water, nor carbonic acid, nor any other vapour or gas in the atmosphere, save and except ozone, could cut off the sun's rays at almost the same wave-length, and ozone must, therefore, be considered to be the cause of the limitation of the solar spectrum (*Journ. Chem. Soc.*, 1881, xxxix., 111).

The absorption capacity of ozone by the ultra-violet rays, within the range of wave-lengths 1850 and 3000, was recently measured by Dr. Edgar Meyer with Kreusler's photometer ("Über die Absorption der Ultra-violetten Strahlung in Ozon," Inaugural Dissertation, Berlin, 1903). He detected the absorption band, and located its greatest intensity at almost exactly the same point as was shown by my photographs. He also arrived at the same maximum of absorption.

An analytical problem connected with the composition of the Dublin gas supply was in the first instance solved by the spectrograph. Coal-gas and oxygen burnt together in a blowpipe yielded flame spectra in the photographs of which some of the groups of bands characteristic of cyanogen were identified. Dr. Eder, to whom we are indebted for so many and valuable spectroscopic and photographic researches, expressed doubts as to these bands being due to cyanogen, and accordingly very delicate chemical tests were applied to the coal-gas which proved absolutely the presence of cyanogen compounds in quantity quite sufficient to render its spectrum on a photographic plate.

The Spectrographic Analysis of Alloys by means of the Spark.

The quantitative spectrographic analysis of articles of ancient jewellery and coins is performed without removing any visible portion by cutting, filing, or dissolving in acids. Here are three examples of a Roman coin with the inscription Augustus Fortunatus, a Greek one of Alkibiades, and an obsolete French coin. The method of spectrographic analysis is extremely simple. A spark is passed from the coin to a piece of graphite and its spectrum photographed. The lines of the metals present are identified by comparison with the spectra of pure substances. The wave-lengths of the lines are measured, and the lines belonging to the different constituents are sorted out. The lines recorded indicate the composition of these two coins.

The Roman coin is a fine bronze, containing copper and tin with a trace of iron. The Greek one is peculiar, as, besides copper and tin, it contains lead and a larger proportion of iron. The coin itself has a peculiar golden colour. The composition of the "sou blanc" is of interest, as in some particulars it resembles the Greek coin. Neither tin, gold, nor silver was found—in fact, the coins were remarkably free from the latter metal. Its percentage composition is—lead, 13.96 per cent; copper, 72.35 per cent; zinc, 12.70 per cent; and iron, 0.85 per cent.

An alloy of this composition was made in the laboratory and rolled out; its spectrum corresponded exactly with that of the coin, in the length, strength, and number of lines belonging to the respective metals. The quantitative composition of the alloy was then determined by the usual methods of chemical analysis, and the spectrographic analysis was proved to be correct.

The metal is peculiar, inasmuch as its composition is that of brass with one-third of the zinc being substituted by lead. It is apparently the large proportion of lead which gives the coin a golden colour, but prevents it having any metallic "ring." It may be remarked that the chief difference between the Greek and Roman coins is the quantity of lead in the former, and this diminishes the proportion of the copper.

A very troublesome piece of work was an investigation into the composition of brittle platinum, the metal being in the form of thin wire in pieces not exceeding 2 m.m. in length. Such fragments could not be held in metal clips for the passage of the spark, because the spark of the platinum would be contaminated by that from the clips. The difficulty was overcome by fusing pure gold wires on to the end of the platinum with a blowpipe flame, and with

the gold wire as a conductor the spectrum of platinum was obtained free from any other metal. If the spark by accident happened to pass from the gold, the gold lines were easily recognised and eliminated from the platinum spectrum. Ten platinum pins were examined, and the metal was proved to be free from any metallic impurity. From other evidence it was shown to be probable that the brittleness was caused by the presence of phosphorus. This investigation proved in a forcible manner—(1) the utility for practical purposes of spectrographic analysis by means of the spark; (2) the importance of determining the wave-lengths of arc and spark lines of pure elements with extreme accuracy; and (3) the advantage of being able to distinguish between two spark lines of very nearly the same wave-length by the difference in their characters.

Spectrographic Analysis of Minerals by means of the Oxyhydrogen Flame.

By means of Deville's blowpipe samples of various metallic elements and their compounds are easily volatilised, and may be submitted to direct spectrographic analysis. The spectra are quite different in character from those of the spark, particularly those of the metalloids and many of the metals, such as lead, tin, copper, silver, gold, antimony, and bismuth.

Iron, cobalt, and nickel give large numbers of lines, which are a characteristic feature in the spectra of meteorites. A collection of materials from iron smelting works, with a hundred and seventy iron ores and associated minerals from every part of the world were examined by Mr. Ramage (formerly of the Royal College of Science) and myself. Unsuspected and uncommon elements were found very generally distributed through these ores in small quantities; for instance, lead, silver, copper, chromium, and nickel, also the rarer metals, rubidium, caesium, gallium, indium, and thallium. This last element is of rare occurrence in oxide ores, but is frequently found in pyrites (*Trans. Chem. Soc.*, 1897, pp. 533 and 547; and 1900, p. 61).

Gallium was found in twenty-one out of fifty-one clay ironstones, and in all aluminous minerals, such as clays and bauxites, even corundum. The siderites (ferrous carbonates) contain indium but no gallium, and the magnetites contain gallium but no indium. The red hæmatites are remarkable above all other iron ores for their purity.

From 375 grms. of the blast-furnace iron from the North-Eastern Steel Works at Middlesbrough, in Yorkshire, there was extracted 0.0235 gm. of gallium sesquioxide. Undoubtedly the richest source of gallium now known is the pig-iron and steel rails made in the Cleveland district of Yorkshire. It contains one part of metallic gallium in from 30,000 of iron.

The thermo-chemistry of the Bessemer process was studied by photographing the spectra of the flames issuing from the mouth of the vessels in which molten raw iron is converted into steel. The flames exhibit peculiarities in different works according to the variations in the process and the materials used. Photographs being taken every successive half minute, the lines were seen to become increased in number, length, and strength as the "blow" progressed, and the temperature of the metal and the flames increased largely.

The Examination of Atmospheric Dust.

In 1874, Baron A. E. Nordenskiöld described three different kinds of dust collected by him. Two of these, which were found on the ice in the Arctic regions, were evidently of terrestrial origin, and could be accounted for, but the third variety was quite different, and appeared to be of cosmic origin. He arrived at the conclusion that this was meteoric dust, and that such was continually falling.

Small quantities of matter which had been precipitated from the atmosphere in snow, hail, and sleet, were submitted to spectrographic analysis by Mr. Hugh Ramage and me, and it was found that they contained the metallic constituents of meteorites. Pumice from the eruption of

Lines in the Spectrum of Argon Photographed by Hartley and Adeney in 1884, compared with those of Crookes and of Eder and Valenta measured in 1895-96.

Crookes, 1895.		Hartley and Adeney, 1884. Hartley, 1887-1890.		Eder and Valenta, 1895-6.	
Blue. Wave-lengths.	Red. Wave-lengths.	Wave-lengths.	Description.	Wave-lengths.	
—	4629·5	4628·9	Strong	4628·60	{ 4609·74 } Two lines; the mean { 4602·63 } is 4606·72.
4608	—	4605·6	Weak	4609·74	
—	4594·5	4595·0	Weak	4602·63	
—	4586·0	4589·3	Weak	4596·30	
—	4534·5	4543·4	Faint	4590·05	
4509·5	4509·5	4506·6	Weak	4545·26	
—	4478·3	4476·6	Weak, fine	4503·15	
—	4426·5	4425·9	Weak, nebulous	4475·15	
—	4399·5	4402·6	Faint	4426·16	
—	4376·5	4378·0	Faint	4401·19	
—	4348·5	4348·2	Strong	4379·79	
4345·0	4345·0	4343·9	Weak, fine	4348·11	
4333·5	4333·5	4335·9	Faint	4343·90	
—	—	4330·8	Faint	4335·42	
4300·5	—	4302·0	Very faint	4331·35	
—	4277·0	4275·3	Faint, nebulous	4304·03 (Kayser).	
—	4272·0	4274·3	Very faint, sharp	4275·34	
—	4266·0	4265·4	Very faint	4272·29	
—	4251·5	4253·4	Faint	4266·44 or 4265·80	
—	4228·5	4228·9	Fairly strong, nebulous	4251·27	
—	4198·0	4197·9	Faint, nebulous	4228·27	
—	4191·5	4189·3	Weak, sharp	4198·40	
—	(4150·5)	4157·9	Very faint, nebulous	4190·85	
4131·5	—	4132·8	Fairly strong, fine	4158·60	
4105·0	—	4104·3	{ 4102·6 } Fairly strong, fine	4131·95	
—	—	4102·6		4104·90 or 4104·10	
4072·5	—	4071·4	Strong, fine	4072·18	
4033·0	—	4034·4	Weak, nebulous	4033·99	
3967·8	—	3967·3	Faint, fine	3968·50	
3943·5	—	3944·5	Faint, nebulous	3944·50	
3931·8	—	3933·9	Very faint	3932·71	
3928·5	—	3929·0	Very faint	3928·78	
3892·0	—	3892·4	Very faint	3892·15	
3851·5	—	3850·0	Faint, fine	3850·70	
3803·5	—	3804·0	Faint, fine	3803·38	
3780·8	—	3782·1	Faint, fine	3781·50	
3770·5	—	3771·5	Faint, fine	3771·58	
3738·5	—	3739·7	Very faint, fine	3738·04	
3729·8	—	3726·6	Strong, fine	3725·67 (Kayser).	
3587·0	—	3589·6	Weak, fine	3588·94	
3580·3	—	3583·7	Weak, fine	3582·72	
3575·0	—	3576·2	Weak, fine	3576·80	
3560·0	—	3560·6	Weak, nebulous	3560·15	
3544·5	—	3544·2	Weak, nebulous	3545·78	
3513·5	—	3514·1	Very faint, fine	3514·53	
3490·0	—	3490·7	Weak, fine	3491·71	
3475·7	—	3478·1	Faint, fine	3478·40	
3453·5	—	3456·2	Very faint, fine	3454·30	
3388·0	—	3389·9	Fairly strong, fine	3390·05	
3042·7	—	3042·5	Faint, fine	3046·15	
2734·5	—	2733·2	Faint, fine	2732·67	

Krakatoa, which occurred in 1883, was also examined. Dust which fell into porcelain dishes placed on the grass, open to the sky, contained carbonaceous particles which looked steel-grey and were magnetic. Particles of soot were easily washed away, and the heavier particles were spectrographically analysed. Soot from various chimneys, and flue-dust from chemical and metallurgical works was examined. Several metallic and stoney meteorites were also examined. The dust which had fallen directly from the clouds was distinguished by its regularity in composition; it appeared to contain the same proportions of iron, nickel, calcium, copper, potassium, and sodium. Volcanic dust differed from this in several particulars. Dust from sleet, snow, and hail suddenly precipitated from dark clouds again differed, and the difference was chiefly in the proportion of lead present, which in the dust from sleet was

found to be much larger than in the other specimens. The conclusion arrived at was, that the dust which fell in November, 1897, was certainly meteoric, and that which fell in hail and sleet was of terrestrial origin, and most probably the product of chemical or metallurgical works. It was unlike flue-dust and not like soot in composition. The inference was that some of it was fume, such as is seen rising from the mouth of the Bessemer vessels. It was observed also that some of this dust contained a large proportion of lead.

The works near Dublin are not capable of causing dark patches in the sky at a very great elevation such as were seen before each of these storms. Whence came this fume? These darkening hazes in the sky were noticed always in an easterly or south-easterly direction. In South Wales, in the neighbourhood of Swansea, there is the largest group

of metallurgical works in the United Kingdom, where copper and lead are smelted and refined, and iron ores are smelted and the metal converted into steel. In the Vale of Dowlais clouds of fume arise from the Bessemer converters to a height of 300 or 400 feet in an unbroken column; the fume then rolls over and diffuses into the atmosphere, and with an easterly movement of the air, it disperses itself slowly over a large area, and is borne away across St. George's Channel. Besides the South Wales district we have the manufacturing districts, known locally as the "black country," and "the potteries" of Staffordshire, also the chemical works of Lancashire, all contributing such fume, which passes over the Irish Sea when an easterly wind prevails, and travels into the interior of Ireland.

It might be supposed that the chemical works at the river-side, near Dublin, may have contributed flue-dust, but that was proved not to be the case, for flue-dust from the Dublin chemical works is distinguished by containing the metal indium, and none of the samples of dust from hail, rain, or sleet contained any trace of this element.

Among other questions which have been solved by spectrographic analysis is the cause of the colour in slate. Three varieties were taken from the Bethesda quarry in North Wales, green, reddish purple, and blue in colour. The green colour was found in patches, and in every case where these patches occurred, the colour was undoubtedly due to copper, either as basic carbonate or silicate. The reddish purple slates were found to be coloured by a manganese silicate, and the blue slates, in addition to manganese, contained a notable quantity of cobalt silicate. The direct analyses of galena found in Crossmaglen, Ireland, were made, chiefly to ascertain whether it contained any payable quantity of silver, for the information of the Department of Agriculture and Technical Instruction. Quantities of a gramme were burnt for each photograph, but the lines of silver were so faint that the ore was reported to be of no value. A larger quantity was assayed in the usual manner, and the result led to the same conclusion. Associated with the galena was a cream-coloured massive crystalline mineral which, when spectrographically examined, proved to be very pure lead sulphate containing only a trace of potassium and a little copper, with a total absence of silver.

The unexpected occurrence of nickel in certain rocks, of strontia in a marine boiler incrustation, to the amount of 1 per cent, of lithia, and of beryllia in some of the granites and granitic rocks around Dublin have been proved by spectrographic analysis. For the examination of the absorption spectra of the rare earths, for testing methods for the separation of metals in quantitative analysis, and for determining the composition of small precipitates obtained in the analytic separation of substances, the spectrographic method is invaluable. I venture to predict that when the methods of working, and the practical details are more widely known, the spectrograph will become an indispensable instrument to the chemist, whether engaged in mineral analysis or occupied with organic research. Quartz and calcite are the only materials of use at present; the Jena ultra-violet glass when cut into a prism of 60°, transmits only so far as wave-length 3283 (Cd. 12); with calcite wave-length 2194, and with quartz wave-length 2025, are easily photographed.

Formation of Dipeptides by the Hydrolysis of Proteins.—Emil Fischer and Emil Abderhalden.—On hydrolysing silk fibroin with strong cold sulphuric acid or hydrochloric acid a dipeptide of glycocoll and *D*-alanine is obtained, and can be isolated in the form of anhydride. Similarly, when other proteins are used other dipeptide anhydrides are obtained. Of these the authors have prepared two, one composed of *L*-tyrosine and glycocoll, while the other contains glycocoll and active leucine. The first of these new compounds is glycyl-*L*-tyrosine anhydride, and the second (which was obtained from elastine) is glycyl-*L*-leucine anhydride.—*Berichte*, xxxix., No. 10.

MOLECULAR CONDUCTIVITIES: QUANTITATIVE RELATION.

By PHILIP BLACKMAN.

It was shown by the author that there exists a "Quantitative relation between molecular conductivities" (*Phil. Mag.*, 1906, xi., 416). Out of 195 quantities used in constructing the table in that paper, 185 were drawn from an 1893 edition of Landolt-Börnstein's "Physikalisch-Chemische Tabellen" and the remaining ten from the 1905 edition.

The following table (in which 264 molecular conductivity numbers have been employed for its construction) is entirely constructed from the data in the 1905 edition.

v (at 18°) =	1000	500	200	100	50	20	10	2	1
K'HCl . .	484	473	479	466	472	463	452	422	387
K''HCl . .	475	475	473	471	469	463	454	420	384
K'''HCl . .				470			444	400	367
K' $\frac{1}{2}$ H ₂ SO ₄ . .	468	461	442	426	409	377	350	323	310
K'' $\frac{1}{2}$ H ₂ SO ₄ . .	459	451	433	415	395	368	342	328	304
K''' $\frac{1}{2}$ H ₂ SO ₄ . .				413			332	296	285
K'HNO ₃ . .	485	484	480	478	474	466	458	432	413
K''HNO ₃ . .	477	477	475	473	469	465	458	424	401
K'CH ₃ CO ₂ H .	177	165	154	148	144	138	134	127	122
K''CH ₃ CO ₂ H .	171	160	152	147	144	141	139	127	117
K' $\frac{1}{2}$ H ₂ C ₂ O ₄ . .	292	284	276	273	260	250	235		170

$$K'HCl = \mu v_{HCl} + \mu v_{KOH} - \mu v_{KCl}$$

$$K''HCl = \mu v_{HCl} + \mu v_{NaOH} - \mu v_{NaCl}$$

$$K'''HCl = \mu v_{HCl} + \mu v_{LiOH} - \mu v_{LiCl}$$

$$K'\frac{1}{2}H_2SO_4 = \mu v_{\frac{1}{2}H_2SO_4} + \mu v_{KOH} - \mu v_{\frac{1}{2}K_2SO_4}$$

$$K''\frac{1}{2}H_2SO_4 = \mu v_{\frac{1}{2}H_2SO_4} + \mu v_{NaOH} - \mu v_{\frac{1}{2}Na_2SO_4}$$

$$K'''\frac{1}{2}H_2SO_4 = \mu v_{\frac{1}{2}H_2SO_4} + \mu v_{LiOH} - \mu v_{\frac{1}{2}Li_2SO_4}$$

$$K'HNO_3 = \mu v_{HNO_3} + \mu v_{KOH} - \mu v_{KNO_3}$$

$$K''HNO_3 = \mu v_{HNO_3} + \mu v_{NaOH} - \mu v_{NaNO_3}$$

$$K'CH_3CO_2H = \mu v_{CH_3CO_2H} + \mu v_{KOH} - \mu v_{CH_3CO_2K}$$

$$K''CH_3CO_2H = \mu v_{CH_3CO_2H} + \mu v_{NaOH} - \mu v_{CH_3CO_2Na}$$

$$K'\frac{1}{2}H_2C_2O_4 = \mu v_{\frac{1}{2}H_2C_2O_4} + \mu v_{KOH} - \mu v_{\frac{1}{2}K_2C_2O_4}$$

The above table, in conjunction with the following table of percentage "Relative Strengths of Acids" (*CHEMICAL NEWS*, 1906, xciii., p. 284), has been used in the calculation of the "Atomic Conductivities of the Ions" (*Phil. Mag.*, 1906, xii., p. 150).

v (at 18°) =	1000	500	200	100	50	20	10	2	1
HCl . .	100	100	100	100	100	100	100	100	100
HNO ₃ . .	99.4	99.4	99.3	99.5	99.2	99.2	99.7	99.0	100
$\frac{1}{2}$ H ₂ SO ₄ . .	95.9	93.4	88.5	80.5	77.9	70.3	64.1	62.4	62.6
$\frac{1}{2}$ H ₂ C ₂ O ₄ . .	48.0	46.0	43.9	42.7	38.9	36.9	33.3	23.2	19.8
CH ₃ CO ₂ H .	10.9	8.0	5.4	3.9	2.8	1.8	1.3	0.6	0.4

East London Technical College,
London, E.

Sale of Widnes Chemical Works.—The business and plant of Hadfields, Ltd., Chemical Manufacturers, of Weston Point, Cheshire, was put up for auction on Sept. 20th by Mr. George Gaunt, of Liverpool, acting on instructions of Mr. T. S. Sheard, the Receiver appointed by the Court of Chancery. It was sold as a going concern for the sum of £2500. The business and property had been for some time past for sale by private treaty, but no "deal" was arrived at. The auction was interesting as a practical test of value. A number of buyers from all parts of the Kingdom attended with a view of picking up details, but the sale *en bloc* prevented their object being attained.

THE DETERMINATION OF SILICA.

By N. KNIGHT and F. A. MENNEKE.

DOLomite rock (containing silica) and ores of iron and manganese were treated with different acids as solvents, and the resulting insoluble residue was studied. The purpose of the work was to ascertain the treatment which would leave the smallest amount of residue, and therefore the purest form of silica. In some cases the nature of the residue other than silica was investigated.

Each specimen studied was finely ground with agate mortar and pestle, until the powder did not feel gritty when placed between the teeth, and was then thoroughly mixed. About a grm. of the powder was used in each determination.

Siderite.

1. *a.* The powder was placed in a beaker and covered with a watch-glass. It was dissolved with pure dilute hydrochloric acid (equal parts hydrochloric acid of sp. gr. 1.20 and water) by carefully heating to boiling. The insoluble residue was found to be 6.06 per cent. This was transferred to a weighed platinum crucible and treated with sulphuric and hydrofluoric acids; the loss of weight, representing the silica, was 1.44 per cent. A blank test was made of the sulphuric and hydrofluoric acids used, and no residue was left on their evaporation. The filtrate from the insoluble residue was evaporated on the water-bath, and as crystals began to appear the mass was stirred with a glass rod flattened on the end, until a fine dry powder resulted. This, on treatment with concentrated and dilute hydrochloric acid and afterwards with water, gave no residue.

b. A grm. of the fine powder was placed in a small porcelain evaporating dish and dissolved on the water-bath with dilute hydrochloric acid. It was stirred to a fine dry powder, as in the filtrate under *a*. This, on receiving the usual treatment with hydrochloric acid and water, gave an insoluble residue of 6.07 per cent. After treatment with sulphuric and hydrofluoric acids, 1.45 per cent of silica was shown to have been present. The residue in the crucible, which had the appearance of iron, was dissolved in concentrated hydrochloric acid and the iron precipitated with ammonia; 4.64 per cent Fe_2O_3 was obtained. This comparatively large amount of insoluble residue, practically the same by both tests, was somewhat of a surprise. The amounts of the iron oxide and silica are not in the proper ratio to form a silicate; or, at best, only a portion is silicate, the rest seems to be iron oxide in such a condition as not to be acted upon readily by hydrochloric acid. The next two experiments tend to confirm this view.

c. Method *a* was repeated, except dilute nitric acid (equal parts nitric acid of a specific gravity of 1.42 and water) was substituted for the hydrochloric acid. This leaves a much smaller and lighter coloured portion than the hydrochloric acid. The insoluble residue was 1.336 per cent, which proved to be 1.30 per cent silica. On evaporating the filtrate to dryness, a second portion of insoluble residue was not obtained.

d. Method *b* was repeated, using dilute nitric acid. The insoluble residue was 1.30 per cent, the silica being 1.28 per cent. On second evaporation no residue appeared.

The experiments were repeated, using dilute sulphuric acid. The results were unsatisfactory, as the residues obtained were abnormally large, confirming the well-known fact that the ores of iron are not easily soluble in sulphuric acid.

A complete analysis of this specimen of ore resulted as follows:—

Fe_2O_3		52.59
FeO		4.20
MnO		3.30
MgO		2.68
CaO		0.82
SiO_2		1.45
CO_2		35.00
		100.04

2. Another specimen of siderite was examined and treated by each of the four different methods described in the foregoing. The following figures were obtained:—

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
Residue (per cent) ..	1.33	1.26	0.85	0.94
SiO_2 (per cent) . .	0.91	0.86	0.80	0.85

The residue was obtained by evaporating the filtrates in the foregoing experiments.

3. A third specimen of siderite was available for examination, and it was subjected to the same treatment as before, with the following results:—

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
Insoluble residue (per cent) .	0.40	0.36	0.40	0.38
SiO_2 (per cent) .. .	0.36	0.31	0.35	0.32

The three specimens were purchased of the dealers, and we regret our inability to give the locality from which they were obtained.

Dolomite.

(Specimens from Linn County, Eastern Iowa).

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
1. { Insoluble residue (per cent) ..	0.83	0.89	0.88	0.83
{ SiO_2 (per cent) .. .	0.50	0.64	0.62	0.60
2. { Insoluble residue (per cent) ..	0.54	0.55	0.58	0.56
{ Silica .. .	0.41	0.42	0.41	0.41

When the dolomite is treated with nitric acid, it is impossible to stir the substance to a dry powder, the large amounts of calcium and magnesium nitrates interfering seriously with the drying.

In the following determinations, a second portion of residue was obtained in nearly every case. It was impossible to dissolve the substances in nitric acid, and aqua regia was substituted. The results from the different methods are not all concordant.

Hamatite.

	<i>a.</i>	<i>b.</i>	<i>c</i> (aqua regia).
Residue (per cent) .. .	2.26	2.52	3.19
Residue from filtrate (per cent)	0.71	0.22	0.00
Silica from first residue (per cent)	1.94	2.23	—
Silica from second residue (p. c.)	0.65	0.22	—
Total silica obtained (p. c.)	2.59	2.45	2.90

Magnetite.

	<i>a.</i>	<i>b.</i>	<i>c</i> (aqua regia).
Residue (per cent) .. .	5.76	6.47	11.69
Residue from filtrate (per cent)	0.96	0.30	0.30
Silica from first residue (p. c.)	1.44	2.53	3.09
Silica from second residue (p. c.)	0.96	0.30	0.30
Total silica (per cent) ..	2.40	2.83	3.39

Limonite.

	<i>a.</i>	<i>b.</i>
Residue (per cent) .. .	2.25	3.68
Residue from filtrate (per cent) .	1.66	0.12
Silica from first residue (per cent) ..	2.12	3.52
Silica from second residue (per cent)	1.40	0.12
Total silica (per cent) . . .	3.52	3.64

A Specimen of Commercial Manganese Dioxide.

	<i>a.</i>	<i>b.</i>
Residue (per cent) .. .	12.76	13.95
Residue from filtrate (per cent) . .	1.32	0.12
Silica from first residue (per cent) ..	7.56	7.81
Silica from second residue (per cent)	0.42	0.12
Total silica (per cent) . . .	7.98	7.93

A Specimen of Pyrolusite.

	<i>a.</i>	<i>b.</i>
Residue (per cent) .. .	12.79	14.79
Residue from filtrate (per cent) . .	1.60	0.19
Silica from first residue (per cent) ..	7.92	7.92
Silica from second residue (per cent)	0.28	0.19
Total silica (per cent) . . .	8.20	8.11

In the case of the siderites and dolomites studied, the simpler method gives results fairly concordant with the more complicated method, and the former is therefore to be preferred. A second evaporation and stirring to a dry powder gave no residue and added nothing to the value of the results. Nitric acid as a solvent of the siderites gave smaller residues than the hydrochloric acid treatment.

It is possible, as Hillebrand has pointed out (*Journ. Am. Chem. Soc.*, Nov., 1903), that, even after a second evaporation and filtration, silica may be precipitated with the iron and alumina. To obtain this amount, fusion of the iron and alumina precipitates with acid potassium sulphates and subsequent digestion with water and sulphuric acid are necessary. When the silica content of the specimen is only a few per cent, the amount that would persist in solution would necessarily be small; it would be greater in case of a determination by an alkaline fusion.

With the ores of iron other than siderite that were studied, as well as the specimens of manganese dioxide, the shorter method (simply dissolving in hydrochloric acid) gave, as a rule, as satisfactory results as the longer one.

Cornell College, September 18, 1906.

NOTES ON AN ALLOTROPIC FORM OF ARSENIC AND ON THE ESTIMATION OF ARSENIC WHEN IN MINUTE QUANTITIES.*

By WILLIAM THOMSON, F.R.S.E., F.I.C.

(Concluded from p. 157.)

Influence of $\frac{1}{2}$ c.c. HNO_3 on the Detection of Arsenic in the Form of As_2O_5 , by the Electrolytic Apparatus when using Cathodes of different Substances.

A SOLUTION was prepared containing 0.00000083 grm. of As_2O_5 in each c.c. One c.c. is equivalent to 1/1000th of a grain of As_4O_6 per gallon when using 50 c.c. of the liquid; 10 c.c. of this solution were mixed with $\frac{1}{2}$ c.c. HNO_3 , and introduced into the apparatus, using cathodes of different substances. The cathodes used were graphite, lead, cadmium, zinc, and iron.

After the current (3 ampères) had run for forty-five minutes the arsenic mirrors obtained were approximately equivalent to the following c.c. of the standard solution:—

(The mirrors obtained when HNO_3 is present are very irregular, and only admit of an approximate estimation. In each case the number of c.c. is given as the nearest whole number, and the figures represent averages from a number of experiments).

	C c of standard solution
Graphite	1.0
Lead (a)	6.0
Cadmium	2.0
Zinc	4.0
Iron	2.0

(a) Another lead cathode made by ourselves gave practically the same result, although the results showed some difference.

It is remarkable that the arsenic acid was reduced by each of the different cathodes to the condition of arseniuretted hydrogen in presence of nitric acid or some nitrous compounds, some of which remained intact after the experiment, and that lead was the most efficient.

Influence of different Cathodes on Arsenious Acid.

For this series of experiments a standard solution was prepared containing 0.0000007154 grm. of As_4O_6 per c.c.. One c.c. is equivalent to 1/1000th of a grain

per gallon when working on 50 c.c. of the solution, and 10 c.c. of the standard solution were used for each experiment, which was carried out during forty-five minutes, in each case with a current of 3 ampères.

The mirrors obtained during forty-five minutes were equivalent to the following c.c. of the 10 c.c. of the standard solution taken—the mirrors obtained with a pure zinc cathode during forty-five minutes being taken as the standard:—

	C.c. of standard solution.
Graphite	9
Lead	10
Cadmium	3
Zinc	10
Iron	8

Influence of different Cathodes on Arsenic Acid Solution.

Each c.c. of the standard solution used contained 0.00000083 grm. As_2O_5 (= 1/1000th of a grain of arsenic trioxide per gallon when using 50 c.c.).

The experiments were made as before with 10 c.c. of standard solution, and the time and electrical current as above mentioned. The resulting mirrors obtained were as follows in equivalents of c.c. of the standard arsenic trioxide solution:—

	C.c. of standard solution.
Graphite	1
Lead	9.0
Cadmium	2.5
Zinc (a)	9.0
Iron	5.0

(a) In working with As_2O_5 the 9 parts would be represented by the standard mirrors as 10 for that time of the experiment.

The iron electrode was made by wrapping closely round a glass tube pure fine iron wire, such as is used for making standard solutions.

Part of the arsenic seems to combine with the iron, and to form such a combination that it is not eliminated as AsH_3 when the current is passed. When iron which has previously been used in an arsenic test is used immediately afterwards with acid free from arsenic, it gives a perfect blank after working for forty-five minutes, but on being left till the surface oxidises, and then repeating the test with pure acid, a mirror of arsenic is obtained.

Insensitive Zinc in the Marsh-Berzelius Apparatus.

When zinc contains small quantities of iron, &c., it becomes insensitive when used in the Marsh-Berzelius apparatus, i.e., it gives off hydrogen free from arseniuretted hydrogen, and even when minute quantities of arsenic are added it still fails to produce a mirror. Chapman and Law (*Analyst*, January, 1906, vol. xxxi., p. 358) say that it is due to the hydrogen being given off at a lower electrical supertension, owing to the metal, existing as an impurity, being capable of liberating hydrogen at such lower supertension. They say, however, if 2 grms. of cadmium sulphate be added to the solution, that the insensitive zinc becomes sensitive. It seems remarkable that a metal such as cadmium, which liberates hydrogen at a lower supertension than zinc, should have the effect of doing away with the influence of the iron; in other words, that the deposition of cadmium in a spongy condition on the zinc (which is the metal dissolved by the acid) should have the effect of raising the supertension at which the hydrogen is evolved whilst the iron still remains and must presumably act as it did before the addition to it of a spongy covering. I have repeated his experiment with a sample of electrolytic zinc prepared by Brunner, Mond, and Co., which contains a small proportion of metallic iron. It retains minute quantities of arsenic added to the sulphuric acid used in the Marsh-Berzelius apparatus. We added 2 grms. of cadmium sulphate to this zinc, as recommended by Chapman and Law, and tried experiments by introducing minute quantities of arsenic into the apparatus, with and

* A Paper read before the Manchester Literary and Philosophical Society, March 13, 1906. From *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, vol. 1, Part III.

without cadmium sulphate, but we failed to find that the cadmium sulphate made any difference. The cadmium was thrown down on the zinc, and the evolution of hydrogen much reduced thereby, but in our hands it remained as insensitive as it was before, although the strength of the sulphuric acid was increased so as to give about the same flow of hydrogen.

Chapman and Law mention, as I previously found, that magnesium is insensitive. I endeavoured to obtain magnesium free from arsenic and antimony, but failed. I took, however, the sample which contained the smallest quantity of arsenic, and made the test by dissolving completely 1.4 grms. of magnesium. The experiment was repeated with the addition to it of 0.2 gm. cadmium sulphate. In the latter case a slightly larger mirror was obtained than in the former. Four c.c. of the standard arsenic trioxide solution was then added with 1.4 grms. of magnesium, and a mirror obtained equivalent to from 2 to 2½ c.c. On repeating the experiment with the addition of 0.2 gm. cadmium sulphate, a mirror equivalent to 4 c.c. was obtained.

I dissolved 0.5 gm. of nickel in 100 grms. of pure zinc, and tried this alone; it gave no mirror. I then added 4 c.c. of standard As_2O_3 solution, and it gave a mirror equal to that obtained when pure zinc is employed in the manner previously recommended by me (*British Food Journal*, vol. iv., Nos. 44 and 45). On repeating this with the addition of 0.2 gm. of cadmium sulphate a mirror of about the same size was obtained. Even 1 c.c. of the standard solution (which is equivalent to 0.00000714 gm. of As_2O_3) gave the full mirror. Thus the zinc nickel alloy was quite as sensitive as pure zinc, although it dissolved much more readily in the sulphuric acid, and the addition of 0.2 gm. of cadmium sulphate made no difference in the size of the mirrors obtained.

We then made alloys of zinc with 0.5 gm. of cobalt, iron (in the form of wire), and copper respectively, and of these iron showed the most marked retention of arsenic, for from 20 c.c. of standard arsenic solution a mirror equivalent to about 3 c.c. was obtained, whereas cobalt and copper gave mirrors corresponding with about 20 c.c. in each case.

The addition of 0.2 gm. of cadmium sulphate increased the sensitivity of the iron alloy, a mirror equivalent to about 10 c.c. being obtained from 20 c.c. of the standard arsenic solution.

It seems to me that the action of cadmium sulphate in rendering zinc and other metals more sensitive in the determination of arsenic in the Marsh-Berzelius apparatus must be further studied.

I have pleasure in stating that I am indebted to the care and ability which has been shown by my assistant, Mr. Edwin Hopkinson, M.Sc. (Vict.), in carrying out these experiments.

MAGNESIUM PERMANGANATE AS AN OXIDISING AGENT.

By ARTHUR MICHAEL and WIGHTMAN W. GARNER.

THE use of potassium permanganate, in aqueous solution, carries with it the formation of a strong alkali, which may act in an undesired manner on the substance to be oxidised, or on the products formed in the oxidation. To obviate this difficulty it has been suggested to carry out the process in the presence of a current of carbon dioxide; or, to add magnesium chloride to the oxidising mixture and in this way render the caustic alkali inert, inasmuch as it should at once react with the chloride and form the comparatively inactive magnesium hydroxide (Lossen, *Liebig's Ann. Chem.*, cci., 370). A simpler way would be to employ magnesium permanganate as the oxidiser; moreover, the decided tendency of magnesium salts to pass over into magnesium hydroxide when heated with water, seemed to indicate that this salt should possess an unusual capacity for oxidation.

Magnesium permanganate was first prepared by Mitscherlich ("Gmelin-Kraut," *Anorg. Chem.*, II., 2, p. 527), and later examined in his laboratory by Aschoff (*Ibid.*). They obtained the salt by treating an aqueous solution of barium permanganate with magnesium sulphate, or the corresponding silver salt with magnesium chloride, and describe it as a deliquescent, crystalline substance, with 6 molecules of water of crystallisation. Recently it has been prepared by Chambliss (Dissertation, Johns Hopkins University, 1900), by treatment of permanganic acid with magnesium hydroxide; he found that when heated on a water-bath, in aqueous solution, it is rapidly decomposed, giving off oxygen and ozone, and he also called attention to the strong oxidising power of such a solution.

We first prepared the salt by treating silver permanganate suspended in hot water with an equivalent quantity of magnesium chloride. The first method of Mitscherlich, however, gave better results. Barium permanganate (this salt is now a commercial product) was prepared from the potassium salt, according to the method of Muthmann (*Ber.*, xxvi., 1016); the aqueous solution of the barium salt thus obtained was standardised by means of oxalic acid, and the barium precipitated by the addition of the necessary quantity of magnesium sulphate. The filtrate from the barium sulphate was evaporated on the water-bath to dryness. The product thus obtained has a crystalline structure and bluish grey lustre. In order to completely dehydrate the salt it was heated at 100°, in a vacuum, for several days, and it appeared to undergo but little decomposition by this treatment. Its metallic lustre was not wholly lost, though its colour changed from blue to a purplish tint, resembling that of the potassium salt. (A sealed tube containing some of the salt exploded during the summer, although it was kept in diffused light).

We found anhydrous magnesium permanganate to be insoluble in chloroform, carbon tetrachloride, benzene, toluene, nitrobenzene, ligroin, ether, and carbon bisulphide, and without action on these compounds at ordinary temperatures, unless some solvent was added to bring about solution of the salt. Methyl alcohol dissolves it in considerable quantity, forming a solution which is tolerably stable at ordinary temperatures, while ethyl and propyl alcohols are attacked instantly. The methyl and ethyl esters of acetic acid dissolve the salt to some extent, and form comparatively stable solutions. It also dissolves quite readily in glacial acetic acid, and the solution remains unchanged after several hours at room temperature. Propionic acid is attacked more readily, while butyric and isovaleric acids are decomposed with violence and with evolution of carbon dioxide. Acetone dissolves the salt, but is at once attacked with considerable evolution of heat. By way of comparison, it may be mentioned that Peau de Saint-Gilles (*Ann. Chim. Phys.*, [3], lv., 396) found that potassium permanganate is fairly soluble in acetone, and the solution is quite stable even when boiled. (Such a solution has been employed as an oxidising mixture, *vide* Sachs, *Ber.*, xxxiv., 497; Michael and Leighton, *Journ. Prakt. Chem.*, lxxviii., 523). Other aliphatic ketones, which oxidised with difficulty by potassium permanganate, are at once attacked by the magnesium salt; lactic and other hydroxy acids, as well as keto acids, are also immediately destroyed. Of all the solvents examined, only two were found to be sufficiently stable toward the salt to be of any practical use for oxidation purposes, viz., glacial acetic acid and pyridine.

Dissolved in glacial acetic acid, magnesium permanganate is an extremely powerful oxidising agent. When such a solution is added to benzene, surrounded with a mixture of salt and ice, a constant current of carbon dioxide is evolved. This is a striking fact when the extraordinary stability of benzene toward other oxidising agents is taken into consideration. Carius (*Ann. d. Chem.*, cxlviii., 50) oxidised benzene with a mixture of manganese dioxide and sulphuric acid, and succeeded in isolating, besides carbon dioxide, formic, benzoic, and phthalic acids as pro-

ducts of the oxidation, but these organic acids are all instantly destroyed in the cold by magnesium permanganate in acetic acid solution, and we were unable to separate an intermediate product in the oxidation of benzene to carbon dioxide. (Carius used a mixture of 5 parts sulphuric acid to 1 of water, which dissolved some of the benzene. Although he states that no chemical action takes place when the hydrocarbon dissolves, he does not appear to have examined whether a slow chemical action does not occur).

The homologues of benzene show the same conduct towards the solution of the salt as does benzene itself. Moreover, open-chain hydrocarbons, such as hexane, which are also extremely stable towards the usual oxidising agents, are likewise readily decomposed, yielding carbon dioxide.

Potassium permanganate is almost insoluble in glacial acetic acid, but is fairly soluble in acetic anhydride, forming a solution which is only slowly oxidised on standing. (It is considerably more soluble in the anhydride than in acetone). Such a solution is, however, not to be compared with that of the magnesium salt in glacial acetic acid as regards its oxidising power. Benzene, toluene, and hexane are scarcely attacked in the cold, and even ketones are only oxidised with difficulty.

Magnesium permanganate dissolves more easily in pyridine than in glacial acetic acid, but the solution in the former solvent has surprisingly weak oxidising powers. In fact, those compounds, such as alcohol, acetone, and ethyl acetate, which are in themselves solvents for the salt, are acted on less readily in the presence of pyridine than when used alone; that is, pyridine seems to exert an inhibitory influence on the salt as an oxidiser. A solution of the permanganate in a mixture of acetic acid and pyridine is not stable, although either solvent, taken alone, forms a stable solution. Potassium permanganate is also readily soluble in pyridine, but, as in the case of the magnesium salt, the solution shows very weak oxidising powers. Methyl alcohol is more slowly attacked than when treated with the salt alone; acetone is stable, as is also ethyl acetate, while ethyl alcohol is oxidised fairly readily. Quinoline dissolves the magnesium salt, but the solution is unstable, and this base is also slowly attacked in the presence of pyridine.

From the above mentioned experiments it appears that anhydrous magnesium permanganate, in some solvents, completely destroys the benzene ring, while pyridine is attacked with very great difficulty. In the aliphatic series the higher hydrocarbons and their derivatives are oxidised very readily to carbon dioxide, whereas the lower members, particularly in the first two carbon series, are comparatively stable. The importance of the nature of the solvent used is strikingly shown in the cases of glacial acetic acid and pyridine. Not only is the pyridine solution surprisingly stable, but the inhibitory effect of the base in preventing otherwise easy oxidations is difficult to understand, especially as there is no evidence of a chemical union between it and the salt.

These preliminary experiments are suggestive along several lines. It would be interesting to ascertain whether magnesium permanganate, in aqueous solution, would show itself so destructive to aromatic substances as it does in acetic acid. That the aqueous solution will prove of use in case of difficultly oxidisable substances, and in oxidations where it is desirable to prevent the formation of an alkaline solution, seems very probable. (According to Ullmann and Uzbachian, *Ber.*, xxxvi., 1797, the calcium salt does not seem to be a more powerful reagent than potassium permanganate). Again, if substitution products of pyridine are also stable towards the acetic acid solution, the mixture will undoubtedly be of service in the degradation of the many complicated derivatives of the base. The solution of potassium permanganate, in acetic anhydride, may also prove valuable in certain oxidations, as acetic anhydride is not only a ready solvent for many substances that are difficultly soluble in water, but it acts readily on

substances containing a hydroxyl or formyl group, to form products that may be less susceptible to oxidation, and the anhydride may, in this way, to a certain extent, protect the intermediary products of oxidation and enable their isolation.—*American Chemical Journal*, xxxv., No. 3.

THE ESTIMATION OF OPALESCENT SILVER CHLORIDE PRECIPITATES.*

By ROGER CLARK WELLS.

IN a recent paper upon the nephelometer (Richards and Wells, *Amer. Chem. Journ.*, 1904, xxxi., 235), a perfected form of this instrument was described and shown to be well fitted for comparing the scanty precipitates usually called opalescences. By the use of prisms the precipitates in two test-tubes could be viewed in one field of vision, and an accuracy of about 1 per cent was attained in the comparison of nearly equal opalescences. The nephelometer would appear to be a better arrangement than that described by Tswett (*Zeit. Phys. Chem.*, 1901, xxxvi., 450), because the light strikes the tube sidewise, and one can view the whole tube, instead of looking across the tube through which a pencil of light is passed. Some illustrations of the method of estimating chloride in an unknown solution were given and some general precautions mentioned, but a detailed discussion of the phenomena of opalescent precipitates was reserved for a future paper. During the frequent use of the nephelometer in the revision of the atomic weight of sodium and chlorine, the methods of nephelometry were studied and improved until they were sufficiently accurate for the special ends in view (Richards and Wells, *Journ. Amer. Chem. Soc.*, 1905, xxvii., 484). Among the facts which remained to be investigated more thoroughly, however, was the variation of opalescence with time. The present paper contains an account of experiments made upon this subject, as well as upon a great many other points which will widen the range of applicability of nephelometric methods.

Silver chloride is a very suitable salt for studying these questions. Its solubility is small in the ordinary sense, yet large as measured by the nephelometer. The presence of other salts or acids up to concentrations of about N/0.01 does not alter its solubility, or at most only very slightly. In accordance with our present theories of solution the dissolved silver chloride is, on account of the great dilution, completely ionised, and there will be, in general, a concentration of silver and a concentration of chloride which will be equal for only one special case. Moreover, it appears to fulfil the demands of the concentration law (mass action) surprisingly well, for a solution of it can be practically freed from chloride by the addition of sufficient ionised silver and from silver by the addition of ionised chlorine.

The difficulty, in previous work, was the selection of the major variables and the control of these so that only one might be varied at a time. This was a hard problem as long as two tubes were compared with each other, for one could not decide whether the observed relative variation was due wholly to the first, partly to the first and second, or wholly to the second tube. The results of this paper would not have been attained if a constant standard of reference had not been found. At first suspensions of chalk were tried, but they proved even more variable than the opalescences (Ostwald - Luther, "Physico-chemische Messungen," p. 248). Ground glass, however, appeared to be well adapted to the purpose. Ordinary window glass (plate-glass might have been better) was cut into pieces about an inch square, and these were ground by fine emery until a series was obtained which ranged from opacity to transparency. Some were ground on both sides. All were covered by black paper having

* From the *American Chemical Journal*, xxxv., No. 2.

a round hole in the centre about 16 m.m. in diameter. When such a plate was placed upon the top of the sliding tube in the nephelometer, in a definite and reproducible position, it had exactly the appearance of an opalescent precipitate. The slight colour of the window glass only heightened the resemblance. Nearly all the results in this paper, then, were obtained by comparing a single tube of opalescence with a standard glass, and it is evident that the results so obtained are more reliable than the observations published heretofore. Several of the glasses were standardised, after the needful precautions had been learned. For example, one was found by about 20 trials to be equivalent to 15.1 arbitrary units of opalescence, the extremes being 10 and 19. At first sight this does not appear to be at all accurate, but when one reflects that, under improper conditions, the readings might be as high as 45, it appears more satisfactory.

With a constant standard of reference the effect of a great many variations might have been studied. What proved to be major variables proved also to be dependent upon each other. Some of the most obvious influences are the manner of precipitating and stirring the solution. These operations were done as uniformly as possible in all the experiments. Whenever definite, very dilute solutions were prepared, by diluting more concentrated ones, or whenever small quantities of electrolytes were added, the solutions were stirred most thoroughly, and finally allowed to stand for a few minutes to make them still more uniform. During precipitation, also, they were stirred thoroughly and uniformly, usually 20 strokes, with the propeller-shaped platinum stirrers, previously described. More than 20 strokes had no further effect. Failure to stir when precipitation begins results in a noticeable alteration of the intensity of opalescence. Uniform precipitation seems to be hard to attain, but perhaps it might be regulated somewhat by using just the right concentration of precipitant. As regards light, most of these experiments were done in the dim light of a single 16-candle-power light in a dark room. Some were repeated in red light alone, but no difference was detected. When not under direct observation, all tubes stood in a box in absolute darkness. Of course the opalescences darken in daylight, but no darkening was ever certainly proved to be due to the light of the room in which experiments were performed. Even some weak opalescences exposed to the light of the nephelometer for two hours were not darkened perceptibly.

The silver nitrate employed had been sufficiently re-crystallised to free it wholly from chloride. The potassium chloride had been purified by precipitation with hydrochloric acid. The nitric acid used had required three wasteful fractional distillations before it was free from chloride. The potassium nitrate had been evaporated to dryness with the addition of nitric acid until all hydrochloric acid was expelled; it was then re-crystallised from water. The sulphuric acid was boiled. Aluminium nitrate was prepared by dissolving clean strips of the metal in the pure nitric acid. Throughout the work great precautions were taken to get rid of contaminating chlorides from the air, the desk, and the hands. It is a pleasure to thank Mr. William D. Hutchinson, of Oxford University, for his kind assistance in preparing some of the standard solutions, and in making a number of the preliminary observations.

1. Effect of the Medium in which Precipitation Occurs.

When silver chloride is precipitated by mixing fairly concentrated solutions, large curds settle out, and very little opalescence is observed. In more dilute solutions, about normal for example, the addition of a silver salt to a chloride leaves a marked opalescence, but, strange to say, the addition of chloride to the silver salt results in a coagulation, and, consequently, much less opalescence. Ionised silver therefore appears to have marked coagulating power, since it is present in excess during precipitation in the latter case. Precipitation from extremely dilute solutions yields a fine state of division or suspension. This coagulates or clarifies slowly upon shaking, much faster in the presence

of nitric acid. Similarly, during repeated washings of the precipitate in pure water it tends to go into an emulsion or milky state, which will not clear for days, alone, but usually clarifies by the addition of nitric acid. Now nitric acid has been shown to hasten the development of opalescent precipitates also, and one may thus infer that precipitation and coagulation are very closely related. Indeed, it is impossible to draw any line between the two phenomena—precipitation must be a process of coagulation. The object of the nephelometric experiments was therefore to attain this coagulation in a definite and reproducible fashion. It appeared reasonable to suppose that the maximum opalescence which could be attained in any way would most nearly represent the truth. For practical purposes the quickest way to attain that maximum would also be desirable. Hence, it might appear that all experiments should record a study of the speed of precipitation. They should, were it not for the fact that opalescences forming at different rates, in different media, do not necessarily attain the same intensity. Very slow precipitations appear, in general, to be swamped by superimposed effects, so that they never attain the maxima which quickly forming opalescences acquire. The variable to be controlled first in nephelometric observations, therefore, is the medium. In order to point out the effect of various media, the maximum opalescences which could be attained, without regard to the time required to attain the maximum, are here stated. Then, under a separate head, will be shown the speeds attained in the best media.

Intense Opalescences.

KCl (N/0.000040) precipitated by AgNO_3 .

	Intensity of opalescence.
In water	21 (a)
N/0.05 HNO_3	29
N/0.05 $\text{Al}(\text{NO}_3)_3$	29
N/0.025 KNO_3	32

(a) These numbers are merely the reciprocals of the heights of opalescence appearing equal to a glass, multiplied by 1000. They indicate intensity of opalescence on an arbitrary scale.

AgNO_3 (N/0.000040) precipitated by KCl.

	Opalescence.
Without any electrolyte	21
In N/0.025 $\text{Al}(\text{NO}_3)_3$	16
In dilute H_2SO_4	28
In N/0.025 HNO_3	30
In N/0.025 KNO_3	31
In $\text{HNO}_3 + \text{KNO}_3$	26
In $\text{HC}_2\text{H}_3\text{O}_2$	24

The opalescence in water alone would probably not have been so great if the traces of electrolyte produced by metathesis could have been eliminated. Hence the presence of electrolytes appears advantageous in these intense opalescences.

Weak Opalescences.

KCl (N/0.000007) precipitated by AgNO_3 .

In the first experiments about a drop of fairly concentrated solutions of various salts was added to each tube. Tubes without any electrolyte attained the greatest opalescence. This was attributed to a possible greater solubility of silver chloride in the solutions containing electrolytes. It may be related to the coagulative power of ionised silver. With only traces of electrolytes, all the tubes behaved similarly. Further experiments might well be made on this case, with special regard to the proper excesses required, according to the results shown later.

AgNO_3 (N/0.0000040) precipitated by KCl.

	Opalescence.
In water	14
In N/0.025 KNO_3	20
In N/0.025 $\text{Al}(\text{NO}_3)_3$	18
In N/0.025 HNO_3	18
In trace of HNO_3	18

A different glass was used for weak opalescences than for intense opalescences. In this case electrolytes appear to be advantageous as usual.

Experiments were also made with "actual" silver chloride solutions. The phenomena were, in general, similar to the above, except for time effects to be noted later. Nobetter electrolytes than potassium nitrate and nitric acid for intensifying opalescence were found. The quantity to be used depends upon the amount of precipitate; it should be small with slight quantities of precipitate.

It is believed that the excesses used for precipitation in the cases above were sufficient. A full study of that matter had not been made when these results were obtained, and hence less attention was paid to it. Below are given the results bearing upon that particular question.

(To be continued).

NOTICES OF BOOKS.

The Laboratory Book of Mineral Oil Testing. By JAS. A. HICKS. London: Charles Griffin and Co., Ltd. 1906.

THIS short laboratory guide will be useful to those who may occasionally have to test samples of oils, but are not specialists in the subject. It describes what may be called the officially recognised methods of examining mineral oils, and the author's experience in the laboratory of Sir Boverton Redwood, the adviser on petroleum to the Admiralty and Home Office, has given him unique opportunities in practical work, so that his book contains much that will be of value to the analytical chemist. The various methods of determining specific gravity with special reference to oil analysis are fully discussed, and the way to ascertain the flashing-point with the Abel petroleum tester and other testers is explained, while clear directions for measuring viscosity are given, together with a description of the Redwood viscometer. The experimental details are carefully stated, and the standard methods, which are now universally adopted in oil analysis, are fully explained in the book.

Ausführliches Handbuch der Zuckerfabrikation. ("Complete Handbook of the Manufacture of Sugar"). By Dr. A. RÜMPLER. Braunschweig: Friedrich Vieweg und Sohn. 1906.

THE tenth volume of "Muspratt's Encyclopædia of Technical Chemistry" deals with the manufacture of sugar, and is as comprehensive and full of detail as the preceding volumes, which are universally recognised as almost indispensable parts of the equipment of the libraries of works, technical laboratories, and colleges. The author of this volume, Dr. Rümpler, has had long experience in sugar laboratories, and practical details are specially emphasised, complete and clear accounts of the various mechanical appliances being included. The scientific aspect is not neglected, though the chapters on the chemistry of the sugars form one of the least satisfactory parts of the book, even if the difficulty of keeping up to date such a treatise, which takes some time to get through the press, is taken into account. The analytical work in connection with sugar manufacture is treated at some length, all ordinary processes being carefully described, while the structure and cultivation of the sugar-beet, and more shortly of the sugar-cane, are also discussed. The book is undoubtedly a mine of valuable information, and may be regarded as the standard work of reference from a technical point of view.

Elektrolytische Alkalichloridzerlegung mit Flüssigen Metallkathoden. ("The Electrolytic Decomposition of Alkali Chlorides with Liquid Metal Cathodes"). By Dr. R. LUCION. Halle-a-S.: Wilhelm Knapp. 1906.

THE greater part of this book is occupied by the alphabetical enumeration and discussion of specifications of patents

relating to the electrolytic decomposition of alkali chlorides with liquid metal cathodes, taken out in England, France, Germany, Belgium, and the United States. Mercury electrodes are first considered, and some account is given of the theoretical aspects of the subject, and also of the practical difficulties which have to be surmounted, while details regarding cost of plant, output, &c., are included. The Hargreaves-Bird process, in spite of the fact that it possesses some specially interesting features and is a commercial success, is dismissed in a couple of lines, although more attention is paid to the working of the Castner-Kellner method. The second part of the book deals shortly with processes in which fused metallic cathodes are used, and the subject is attacked in the same way as in Part I., although naturally the section is much shorter and the list of patents less extensive.

CORRESPONDENCE.

METHYLATED SPIRIT.

To the Editor of the Chemical News.

SIR,—The Board of Inland Revenue have refused to grant my application for permission to use unmineralised methylated spirits in our chemical laboratory. Will you be good enough to inform me if the refusal is legal, and, if not, what steps I can take to get it rescinded.

We are an ordinary secondary day school under the Board of Education, and we have large science classes—chemistry, theoretical and practical, being taught to nearly three hundred pupils.—I am, &c.,

W. CAMMACK.

George Green's Schools, Poplar, E.,
September 29, 1906.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 10, September 3, 1906.

Determination of the Fusion-points of Alloys of Aluminium with Lead and Bismuth by means of Thermo-electric Pyrometers.—H. Pécheux.—The author determines the fusion-points of lead-aluminium and bismuth-aluminium alloys by means of two thermo-electric pyrometers: one formed of platinum and platinum-iridium (10 per cent iridium), the other of nickel-copper. These he graduates by means of a Deprez-d'Arsonval galvanometer. The curve obtained for the former couple is a parabola, and for the latter three parabolas. To obtain the fusion-points of the alloys, the hot junction of each couple is immersed in a bath of the molten alloy. The spot of light stops in its motion for some seconds when the solidification point is reached. The numbers obtained are between 635° and 652° for lead-aluminium containing 92 to 96 per cent of aluminium, and from 650° to 720° for bismuth-aluminium containing 75 to 94 per cent of aluminium, whilst the melting-point of pure aluminium is between 626° and 630°, as determined by the same method.

Action of Hypiodous Acid in the Nascent State on Acids containing the Ethenylenic Function: Iodated Lactones.—J. Bougault.—The author has already investigated the action of nascent hypiodous acid on certain groups of acids with ethylenic function. Amongst other results, he showed that acids possessing an ethylenic liaison in $\beta\gamma$, $R-CH=CH-CH_2-CO_2H$, give,

under the conditions described, iodated lactones of formula $R-CH-CHI-CH_2-CO$

$\begin{array}{c} O \\ | \\ R-CH-CHI-CH_2-CH_2-CO \\ | \\ O \end{array}$. He has since investigated the ethylenic acids $\gamma\delta$, and has proved that they behave in the same way as the $\beta\gamma$ acids. In this case, however, two iodated lactones are possible,

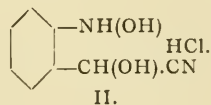
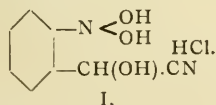
$\begin{array}{c} O \\ | \\ R-CH-CHI-CH_2-CH_2-CO \\ | \\ O \end{array}$ and $\begin{array}{c} O \\ | \\ R-CH-CHI-CH_2-CH_2-CO \\ | \\ O \end{array}$, and hitherto he has

not been able to distinguish between these two. His present research is especially directed towards showing that the presence of an ethylenic liaison in the lactonic situation ($\beta\gamma$ or $\gamma\delta$) is not enough to ensure the formation of iodated lactones, the presence of certain groups in the lactone chain being able to stop the fixation of hypiodous acid.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 10, 1906.

Spectrum of Helium from Radium Bromide.—F. Giesel.—In a radium emanation tube first examined a year ago all the helium lines, besides hydrogen, can be observed as clearly as in a helium tube. The spectrum of this tube was taken with a spectrograph upon a photographic plate, the time of exposure being relatively short (twenty to forty minutes), and by taking the spectra of helium, hydrogen tubes, and the radium emanation tube on the same plate, the resemblances could be readily detected. Thirteen of the helium lines could be easily identified in the spectrum of the radium tube, viz., λ 587.6, 504.8, 501.5, 492.2, 471.3, 447.2, 438.8, 414.4, 412.1, 402.6, 396.5, 388.9, 381.9.

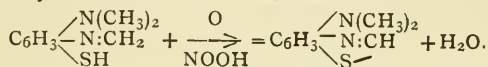
New Reaction Product of the Nitro-group.—Gustav Heller.—Under favourable conditions, when nitro-compounds are reduced to amido-derivatives, nitroso and hydroxylamine compounds appear as intermediate products. Evidently the release of an oxygen atom is not the first reaction which occurs under the influence of the reducing agent, but two hydrogens are attached, and then the nitroso-group is derived from this dihydroxylamine derivative by the elimination of water, $-N \equiv O \rightarrow -N < \begin{smallmatrix} OH \\ OH \end{smallmatrix}$. *O*-nitromandelic acid nitrite, however, gives on reduction with zinc dust and acetic acid in the cold a compound which dissolves in dilute hydrochloric acid at the ordinary temperature without undergoing decomposition, and is separated as hydrochloride by means of fuming hydrochloric acid. This compound behaves like a molecular mixture of the hydrochloric acid salts of *o*-dihydroxylaminomandelic acid nitrile (Formula I). and of a hydroxylaminomandelic acid nitrile of Formula II. The exact way in which the two substances are combined together is not known; the author regards a quinhydrone linkage as most probable, resembling that of isatin with dioxindol to form isatylde.



No. II.

Action of Formaldehyde upon *as*-Dimethyl-*p*-phenylenediaminethiosulphonic Acid, and a New Method of producing Benzothiazoles.—Otto Schmidt.—If formaldehyde is allowed to act in neutral or hydrochloric acid solution upon *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid, the starting point in the manufacture of methylene blue, an unstable amorphous base (anhydroformaldehydedimethyl-*p*-phenylenediamine mercaptan) is

formed. When this is treated with nitrous acid, β -dimethylamidobenzothiazole is formed:—

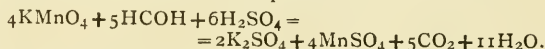


Compounds of Thiosulphuric Acid with Aldehydes.—Otto Schmidt.—The author has found that formaldehyde forms a compound with thiosulphuric acid, and that the compound acid gives with anhydroformaldehydedimethyl-*p*-phenylenediamine mercaptan a well-defined crystalline salt. The formaldehyde-sulphuric acid is not stable in neutral or alkaline solution, the above salt being decomposed partially even on crystallising from hot water. The acid is, however, fairly stable in acid solution. Acidified thiosulphate solutions, to which formaldehyde has been added, only give trithioformaldehyde after standing for some hours. When such solutions are boiled, the acid decomposes almost quantitatively according to the equation $3\text{OH} \cdot \text{CH}_2 \cdot \text{SSO}_3\text{H} = 3\text{SO}_4\text{H}_2 + (\text{CH}_2\text{S})_3$.

Titrimetric Determination of Formaldehyde and Formic Acid by Potassium Permanganate in Acid Solution.—Hermann Grossmann and Arthur Aufrecht.—Lieben's method of estimating formic acid depends upon the fact that, in alkaline solution, it gives with permanganate the following reaction:—



This method has drawbacks; the chief being the difficulty of detecting the end of the reaction, owing to the precipitate of manganese dioxide formed. According to Vanino and Seitter, formaldehyde in acid solution is oxidised to carbon dioxide in the cold, formic acid resulting as an intermediate product. The authors find that this can be applied titrimetrically, allowing the permanganate to act for at least an hour. The equation is—



They think that, in all probability, an intermediate very labile superoxide is formed, which results from one molecule of formaldehyde, as follows:— $\text{HCOH} + \text{O}_2 = \text{H} \cdot \text{C} \cdot \text{OH} \cdot \text{O} \cdot \text{O} \cdot$

It then decomposes very readily, yielding water and carbon dioxide. The oxidation of formic acid proceeds very slowly in the cold, and even in strong sulphuric acid brown manganese dioxide separates out. Twenty-five c.c. of formic acid solution (corresponding to 0.0445 gm. of formic acid) were allowed to stand in a closed flask with 25 c.c. of one-tenth potassium permanganate (3.175 grms. per litre) and 50 c.c. of sulphuric acid (3 parts concentrated acid to 5 parts water). This mixture was allowed to stand a certain time in the dark, and then it was poured into an Erlenmeyer flask, heated to about 40°, titrated with oxalic acid till the red colour and the MnO_2 disappeared, then with $n/10$ permanganate till a faint red coloration was obtained. It was then found that the reaction is complete in about six hours. Salts of formic acid can be titrated as well as the free acid.

Isoconiin, and Synthesis of Coniin.—A. Ladenburg.—The author's experiments have shown that synthetic coniin, prepared from methyl picolylalkyl, is an isomer of *d*-coniin. Though synthetic coniin resembles *d*-coniin in almost all properties, it differs from it in its considerably higher rotatory power (about 4° difference). Synthetic coniin is undoubtedly an individual substance. The conversion of isoconiin into coniin is easily effected by heating it to about 300°.

Decomposition of Azo-dyes with Sodium Hydro-sulphite.—Eug. Grandmougin.—If a solution of Orange II. in water is boiled and sodium hydrosulphite solution added till decolorisation is complete, on filtering and cooling the free amido-naphthol separates out in perfectly colourless flakes. The yield is the same as in the

tin salt method. To reduce benzeneazo- β -naphthol, it is dissolved in alcohol, a saturated aqueous solution of hydrosulphite added to the boiling solution till the colour is removed, and then steam is passed in. Aniline and alcohol pass over, and the amido-naphthol crystallises out from the residue. 2-Benzeneazo- α -naphthol, when treated similarly, yields 2-amido-1-naphthol, and from it the author has prepared the corresponding acetyl products, which had not previously been described. To reduce α -nitroso- β -naphthol by means of sodium hydrosulphite, a solution of the substance in alkali is used. In alcoholic solution azobenzene goes quantitatively into hydrazobenzene when treated with hydrosulphite.

Detection of Ozone with Tetramethyldi- p -diamidodiphenylmethane.—Franz Fischer and Hans Marx.—To detect ozone, and more especially to distinguish it from oxides of nitrogen when it is present only in very small quantity, the authors use paper saturated with an alcoholic solution of tetramethyldi- p -diamidodiphenylmethane. This paper they call tetramethyl-base paper. It is coloured violet by ozone when damp, while oxides of nitrogen colour it straw-yellow. Mixtures of oxides of nitrogen and ozone give dirty brown colorations, between violet and yellow, always supposing that the paper is kept damp. If it dries during an experiment, it may lead to serious errors; thus, dry tetramethyl-base paper is coloured yellow by ozone after about half-an-hour at the temperature of the room. To detect very small quantities of nitric oxide in presence of ozone the current of gases is led into liquid air. The ozone is then dissolved by the liquid air and the nitric oxide separates out in it as blue flakes. It is then only necessary to filter the liquid, when the frozen oxide will be found on the filter, while the ozone can be obtained by boiling the filtrate.

Thermic Formation of Ozone and Nitric Oxide.—Franz Fischer and Hans Marx.—The authors have investigated whether it is possible to produce ozone by thermic means from ordinary gaseous oxygen or from air. They used the following processes:—1. Combustion of hydrogen in air and in pure oxygen. 2. Glowing platinum. 3. Nernst pencils. 4. Arc lights. Their experiments show that the ozone resulting in combustion and heating processes in ordinary atmospheric air or oxygen can be obtained without any sudden cooling by means of liquefied gases. Only a certain velocity of the current of air is necessary. When hydrogen burns in air, hydrogen peroxide and nitric oxide are both formed, as well as ozone. Finally, they have shown that, by regulating the rate of the current of air, it is possible to produce so much ozone and oxides of nitrogen (especially nitric peroxide) that, with water or sulphuric acid, no nitrous acid but only nitric acid is produced.

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THE CHEMICAL NEWS.

VOL. XCIV., No. 2446.

NEW LOW TEMPERATURE PHENOMENA.*

By Prof. Sir JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S.

THE porosity of matter, and the possibility of the occlusion of gases in it, has been the subject of scientific thought for ages. As early as 1674, Boyle, under the title "Suspensions about the Hidden Qualities of Air," writes (Boyle's Works, vol. iii., p. 470, col. 1): "It may not seem altogether improbable, that some bodies we are conversant with, may have a peculiar disposition and fitness to be wrought on by, or to be associated with, some of those exotic effluvia that are emitted by unknown bodies lodged underground, or that proceed from this or that planet. . . . We may be allowed to consider whether among the bodies we are acquainted with here below, there may not be found some that may be receptacles, if not also attractives, of the sidereal and other exotic effluvia that rove up and down in our air." While other matters took up his immediate attention, this one was not lost sight of, for ten years later, in 1684, he returns to the subject in a special discourse, "Experiments and Considerations about the Porosity of Bodies," in which he says (Boyle's Works, vol. iv., p. 206, col. 1):—"When I consider how much most of the qualities of bodies, and consequently their operations, depend upon the structure of their minute and singly invisible particles, and that to this latent contexture, the bigness, the figure, and the collocation of the intervals and pores do necessarily concur with the size, shape, and disposition, or contrivance, of the substantial parts, I cannot but think the doctrine of the small pores of bodies of no small importance to Natural Philosophy." Felix Fontana, the famous physicist to Duke Ferdinand II. of Tuscany, seems to have been the first to have discovered the absorptive power of hot charcoal for gases, a property which he communicated to Priestley, about 1770, and which Priestley confirmed. Lowitz, in 1791, noticed that charcoal decolorised organic solutions. Later experiments were made by Morozzo, and another series of observations were made by two Dutch physicists, Rouppe and Norden. Shortly after this, early in last century, the subject of the action of gases on charcoal was elaborately examined by Theodore de Saussure. Subsequently, Graham and Stenhouse added valuable contributions to the inquiry. The thermal evolutions of some gaseous absorptions in charcoal were determined by Faure and Silbermann; and later, Hunter showed the advantage of using cocoanut charcoal, and made a long series of investigations on the absorption of organic vapours and gases by this variety of charcoal.

In de Saussure's experiment a piece of red-hot charcoal was plunged under mercury, and introduced into the gas to be absorbed after it was cool, without allowing it to come in contact with air. He made use of box-wood charcoal, about which he remarks that it absorbed so little mercury during the cooling that it would readily swim on water. His experiments were conducted at ordinary temperature and pressure, and gave the results in the annexed table, the unit volume being that of the absorbing charcoal. For comparison, similar experiments made by Hunter with cocoanut charcoal are given. (See Table, next column).

He found that even if the charcoal were moistened with water, it was still capable of absorbing one-third to one-half the amount of gas absorbed when quite dry.

During these experiments he called attention to the evolution of heat during absorption, and remarked that it appeared to increase with the absorbability of the gas.

	Boxwood (Saussure).	Cocoanut (Hunter).
Ammonia	90	172
Hydrochloric acid	85	—
Sulphurous acid	65	—
Sulphuretted hydrogen . .	55	—
Nitrous oxide	40	86
Carbonic acid	35	68
Olefiant gas	35	75
Carbonic oxide	9'42	21
Oxygen	9'25	18
Nitrogen	7'5	15
Hydrogen	1'75	4

In further experiments he considered the effect of pressure on the amount of absorption, and found that absorption by volume is far greater in a rare than in a dense atmosphere, but that if reckoned by weight it is more considerable than in the latter than in the former state.

(Saussure's results for carbonic acid may be represented by the formulæ $v = 15'3 + \frac{551'7}{p}$, $v = 19'1 + 0'53p$; where v is the volume absorbed, measured as above, and p is the pressure in inches of mercury).

He continued similar experiments with meerscham, asbestos, and other substances, and also examined the effect of mixed gases.

Hunter examined the absorption of vapours by cocoanut charcoal at or above their boiling-points with interesting and suggestive results as regards selective action. The following table is a selection made from some of his observations:—

Cocoanut Charcoal Absorption of Vapours at Boiling-point of Liquid (Hunter).

Carbon tetrachloride	4
Chloroform	30
Ethyl iodide	36
Alcohol	141
Benzol	59
Carbon bisulphide	117
Ether	87
Ethylamine	127
Water	55

In a note read before the Royal Society of Edinburgh in March, 1874, connected with a research undertaken in association with the late Professor Tait, the absorptive power of charcoal was employed for the first time in the production of high vacua. A piece of cocoanut charcoal was placed in a glass tube, into which were sealed two platinum terminals for electric sparking. The tube was exhausted by the mercury pump, while the charcoal was at the same time heated to a red heat. On sealing off the tube, and allowing the charcoal to cool, the vacuum was so perfect that no spark would pass between the terminals, from a coil giving quarter-of-an-inch sparks in air. Similar experiments were repeated when investigating the theory of the motion of the Crookes radiometer, and are detailed in *Nature* in 1875.

One advantage of charcoal vacua in the study of electric discharges is that on heating the charcoal slowly, and connecting the platinum terminals to the induction coil, the *stræ* may be reproduced and maintained at any degree of rarefaction desired, and as often as we please.

At the Conference on May 24, 1876, in connection with the Loan Collection of Scientific Apparatus at South Kensington, I showed a further simplification and advance in the production of high vacua. A little fluid bromine was placed in a tube, and the tube was put in a water-bath, so that the bromine boiled off. Meanwhile the charcoal in another part of the tube was heated in the usual way, and when all the bromine had been vaporised the tube was sealed off. On the charcoal cooling, it absorbed the

* A Discourse delivered at the Royal Institution, January 20, 1905

bromine so thoroughly that no trace of colour was visible. In this way a vacuum is produced without the use of any exhausting pump.

Although all charcoals exhibit absorptive powers of a high order, nevertheless differences are noticeable. Among charcoals got from wood, the denser woods seem to produce the more absorptive charcoals. Thus box-wood charcoal is more absorptive than fir-charcoal. Saussure found the following relative absorptive powers from different wood charcoals:—

	Sp. gr.	Absorption.
Cork	0.1	Imperceptible.
Fir	0.4	4½ its vol. of air.
Box-wood	0.6	7½ "
Russberg coal (vegetable origin)	1.3	10½ "

But at last the porosity must become so fine that absorption again disappears. Thus, Cumberland black-lead (which is 96 per cent carbon), of sp. gr. 2.17, showed no absorption.

charcoal weighing 0.9565 grm., and thoroughly saturating it with water, he found that it weighed 2.2585 grms. in air, and 0.110 grm. under water. Hence of the gross volume of the charcoal, $\frac{2}{3}$ was occupied by charcoal substance, and $\frac{1}{3}$ was free space into which gases might be absorbed. Saussure found that charcoal at 12° C. and ordinary pressure absorbed 35 times its volume of carbonic acid, but as this occupied $\frac{2}{3}$ of the gross volume of the charcoal, it was actually forced into a space equal to only $\frac{1}{3}$ of its original volume. He concluded therefore that about a third of the gas was liquefied in the pores of the charcoal. From Amagat's observations, the amount liquefied was almost exactly one-fifth).

He found that the cells of charred wood are on an average $\frac{1}{2400}$ of an inch in diameter. Now, if a cubic inch of charcoal were cut up into a number of small equal cubes each of whose edges was $\frac{1}{2400}$ inch, the total area of their surfaces would be 100 square feet, or taking into account the space occupied by the charcoal itself, it would leave about 73 square feet. The thickness of the liquefied

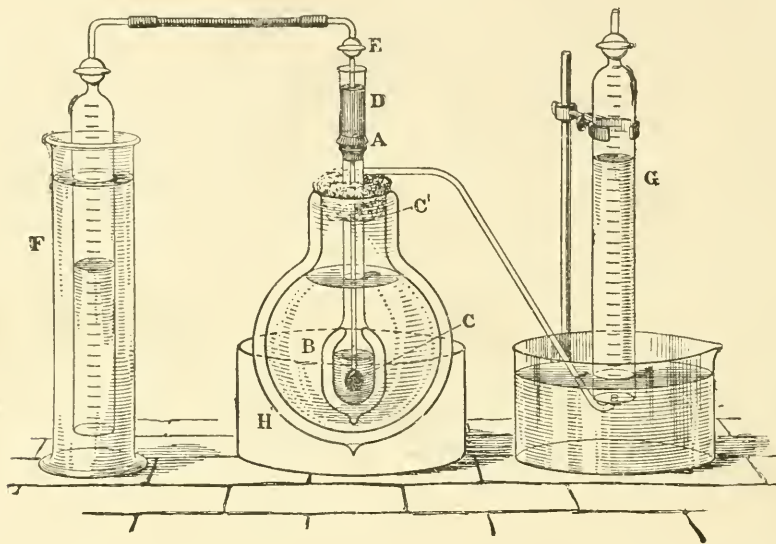


FIG. 1.

From experiments, detailed on a former occasion, undertaken to determine the effect of various substances in a state of fine division placed within the walls of vacuum vessels in protecting the contents of the vessels from external heat, by reason of bad thermal conductivity and the interference of the mean free path of the gas molecules, I found that charcoal and lamp-black were nearly equally good at the temperature of liquid air, and that each was four times as good as graphite. ("Liquid Air as an Analytic Agent," Roy. Inst., April 1, 1898).

From some recent investigations I find that charcoals so different in their origin as cocoanut charcoal and charcoal from cane-sugar differ but little in their absorptive powers for a gas like hydrogen.

NOTE.—Approx.: Series of 30/10/04, range 250 c.c. to 2750 c.c., gave $\log. p = 0.08 + 0.267 c$. (cocoanut); series 4/11/04, range 250 c.c. to 2250 c.c., gave $\log. p = 0.39 + 0.195 c$. (cane-sugar). If $p = 100$ m.m., these give respectively $c = \frac{2.08}{0.267} = 7.8$ (cocoanut) and

$$c = \frac{1.61}{0.195} = 8.3 \text{ (cane-sugar).}$$

Mitscherlich specially studied the nature of porosity in connection with the occlusion of gases. Taking a piece of

carbonic acid over this area would, then, be about 0.000002 inch.

This harmonises to a certain extent with Saussure's remark that denser charcoals, that is, charcoals with pores of smaller diameters, and representing a greater surface for condensation, are the greater absorbers. Nevertheless, we must not forget to notice that the affinities between charcoal and different gases are not the same, and that these will seriously modify any results derived from mere geometrical considerations.

Thermal Evolution and Absorption of Gases by Charcoal at Low Temperatures (Proc. Roy. Soc., 1904; CHEMICAL NEWS, xc., p. 73).

Saussure first observed and roughly noted that the absorption of gases by charcoal at the ordinary temperature gave rise to a considerable evolution of heat. The liquid air and hydrogen calorimeters can be easily arranged to afford an exact measure of the quantities of heat thus given up by the condensation of different gases in charcoal. For this purpose a small glass bulb *c*, containing from half a gramme to a gramme of charcoal, has a long narrow tube *c'* attached, so that it can be immersed in the liquid oxygen, or air in the calorimeter *AB*, while still allowing a part of the tube so project above the cork *A*. The calori-

meter is then inserted in a large vacuum vessel H, containing 2 or 3 litres of liquid oxygen or air, as the case may be, and kept in its place by a loose stuffing of cotton-wool. In order to dry and cool the entering gas (which, in my experiments, did not exceed 40 c.c.), a little annular space is arranged at D, into which liquid air is poured immediately before the experiment begins.

The charcoal, after being placed in the small bulb C, is heated to a low red heat, and simultaneously exhausted by a good air-pump, and after all the gas has been removed, the stopcock E is closed. In this condition it is placed in the calorimeter B.

The experiment is conducted by connecting the end of the tube at E by means of an indiarubber tube with the graduated vessel F containing the gas to be examined. When all is ready the stopcock E is opened, so that the gas may rush into the charcoal, and the heat evolved by its absorption distils off the equivalent quantity of liquid air from the calorimeter B, which is then received and measured in the vessel G.

When we know the constant of the calorimeter—namely, the number of c.c. of gas evaporated by one calorie (about 14.5 c.c. in the present case)—from the readings of the two jars, F and G, we find at once the heat evolved in the condensation per unit volume of gas absorbed. After making a few necessary corrections, the results for different gases are as given in the following table:—

	I. Volume absorbed at 0° C. C.c.	II. Volume absorbed at -185° C. C.c.	III. Ratio of II. to I.	IV. Heat evolved in grm.-calories by absorption at -185° C.
Helium	2	15	7.5	2.0
Hydrogen	4	135	34.0	9.3
Electrolytic gas	12	150	12.5	17.0
Argon	12	175	14.6	25.0
Nitrogen	15	155	10.3	25.5
Oxygen	18	230	12.8	34.0
Carbonic oxide	21	190	9.0	27.5
Carbonic oxide and oxygen .	30	195	6.5	34.5

To render these results comparable, the same specimen of cocoanut charcoal was used for them all, and the numbers in the last column are for absorption by 1 grm. of charcoal. The volumes of the gases absorbed are, both at ordinary and low temperatures, given under standard conditions—namely, 0° C. and 760 m.m. of mercury pressure. If it is desired to know the volumes absorbed at -185° C., when these volumes are measured at -185° C. and 760 m.m. pressure, we have only to divide the numbers in Column II. by three.

In each case, a very remarkable increase of absorption takes place at the low temperature. This is shown in Column III. It is further remarkable that the increase of absorption diminishes, roughly, as the boiling-points of the various gases increase, while Column IV. shows a corresponding increase in the quantities of heat evolved.

The general results are seen best when the values of the thermal evolution and the amount of charcoal involved are reduced to molecular volumes of the condensed gas.

Heat Evolution.

(Charcoal absorption per molecular volume).

	Calories.	Weight of charcoal.
Hydrogen	1600	206 grms.
Nitrogen	3686	180 "
Argon	3636	162 "
Oxygen	3744	160 "
Carbonic oxide	3416	148 "
Carbonic oxide and oxygen	3960	144 "
Electrolytic gas	2414	180 "

Mean, C₁₄M; limit, C₈H₂ and C₁₂He.

A comparison of the molecular latent heats of the

liquefied gases, hydrogen, nitrogen, and oxygen, with the charcoal heat of condensation in each case, is shown in the following table:—

	Molecular latent heats. Calories.	Molecular absorption in charcoal. Calories.
Hydrogen	238	1600
Nitrogen . . .	1372	3684
Oxygen	1664	3744

But perhaps the most striking result is the great difference in properties exhibited by helium. While resembling other cases in showing increased absorption at the temperature of liquid air, the absolute amount occluded is about one-tenth that of the other gases at the same temperature, and the quantity of heat evolved is in even a smaller ratio. We must, however, note that the position of helium on the scale of temperatures, for these experiments, is quite different from that of the other gases, even hydrogen. For helium is being absorbed at a temperature some fifteen times higher than its boiling-point (say, 6° abs.), while in the case of hydrogen this is only four and a-half times its boiling-point (20° abs.). To make a fair comparison, we should take hydrogen at fifteen times its boiling-point, which would bring us up to some 27° C.; that is, the helium absorption at -185° C. should preferably be compared with the hydrogen absorption at 0° C. The inference then is that if we had the absorption of helium at 25° to 30° absolute, we should find it show a still more remarkable condensation than hydrogen does at 90° abs. (183° abs.).

The following experimental results confirm this point of view:—

Helium and Hydrogen.

(Charcoal absorption at the temperatures of boiling and solid hydrogen.)

Temperature.	Helium. Vols. of carbon.	Hydrogen. Vols. of carbon.
-185° C. (b. p. of liquid air) ..	2½	137
-210° C. (liquid air under ex- haustion)	5	180
-252° C. (b. p. of liquid hydrogen)	160	258
-258° C. (solid hydrogen) ..	195	

As the relation between volume and temperature is nearly linear at the lowest portions of either the hydrogen or helium absorption, we may infer that at the temperature of from 5° to 6° helium would be as freely absorbed by charcoal as hydrogen is at its boiling-point, and that in all probability the boiling-point of helium is not below 5° abs. This inference is quite legitimate, because good charcoal at the respective boiling-points of liquid hydrogen, nitrogen, or oxygen, absorbs at atmospheric pressure nearly the same volume of each gas, viz., 260 c.c. per grm.

It is to be noted that the rate of increase of the helium absorption is three times that of the hydrogen, so that a degree or two makes a large increase in the volume condensed. From these results it seems highly probable that the boiling-point of helium is about a fourth that of hydrogen, just as the latter is about one-fourth that of nitrogen.

In Column IV. we get the heat evolved by each gas. These values provide us with still further striking results, for the heat developed is generally greatly in excess of that required for liquefaction. Thus, for hydrogen, whose latent heat at the boiling-point I have recently determined by this calorimeter and found to be 120 grm.-calories, the liquefaction of 135 c.c. of this gas would only evolve about 1½ calories, or one-sixth of that evolved by occlusion in charcoal at the boiling-point of air. Similarly, if we take 51 grm.-calories as the latent heat of oxygen, the liquefaction of 230 c.c. of this gas would produce some 17 calories, or about half of that evolved during occlusion.

(To be continued).

IONIC CONDUCTIVITIES AT 25°.

By PHILIP BLACKMAN.

By aid of the method advanced by the author in "Atomic Conductivities of the Ions" (*Phil. Mag.*, 1906, xii., 150), the conductivities of the ions at 25° have been calculated.* The data (of molecular conductivities of hydrates, acids, and corresponding salts at 25°) are not sufficiently numerous for the purpose of very accurate primary calculations; nevertheless, by taking the average of the respective numbers obtained by all possible substitutions, fairly close approximations to the probable values may have been obtained.

It will be noticed that the conductivities of any ion at dilutions $v = 256$ and 512 are generally almost identical; this would seem to indicate that the maximum conductivity in any case had been attained at dilution $v = 512$, and, consequently, the ionic conductivity of an ion at any dilution above 512 may be taken to be approximately equal to that at 512 °.

v (at 25°) =	32	64	128	256	512
H	350	355	360	360	362
Rb	88	90	94	96	97
Cs	87	90	94	96	97
K	85	86	89	93	95
NH ₄	84	87	90	91	93
Tl	80	85	90	93	93
$\frac{1}{2}$ Pb	56	64	72	76	84
Ag	—	72	74	76	76
$\frac{1}{2}$ Cu	61	63	68	71	71
$\frac{1}{2}$ Ba	59	65	68	70	74
$\frac{1}{2}$ Sr	59	64	67	70	71
Na	60	64	67	69	69
$\frac{1}{2}$ Mg	58	61	65	69	71
$\frac{1}{2}$ Ca	53	63	66	69	70
$\frac{1}{2}$ Ni	56	60	64	69	72
$\frac{1}{2}$ Co	56	58	58	66	69
Li	52	53	56	56	59
OH	150	153	154	154	155
$\frac{1}{2}$ S ₂ O ₆	52	54	59	66	72
NO ₂	56	57	57	58	60
$\frac{1}{2}$ Fe(CN) ₆	45	52	58	61	64
Br	52	53	55	56	57
$\frac{1}{2}$ Fe(CN) ₆	35	43	50	52	65
$\frac{1}{2}$ AsO ₄	41	49	55	58	58
$\frac{1}{2}$ S ₂ O ₃	36	44	49	53	58
Cl	51	52	52	52	53
$\frac{1}{2}$ S ₂ O ₈	42	49	53	54	55
I	48	49	50	50	51
ClO ₄	47	48	49	49	50
NO ₃	44	48	48	48	49
$\frac{1}{2}$ SO ₄	40	42	44	47	50
$\frac{1}{2}$ CrO ₄	40	41	43	46	48
$\frac{1}{2}$ SeO ₄	36	39	41	44	47
MnO ₄	40	41	42	42	43
ClO ₃	38	41	42	42	43
$\frac{1}{2}$ SO ₃	34	38	41	42	43
$\frac{1}{2}$ WO ₄	36	38	40	41	44
$\frac{1}{2}$ PO ₄	—	—	34	39	42
$\frac{1}{2}$ Cr ₂ O ₇	34	35	37	37	39
$\frac{1}{2}$ PtCl ₆	32	36	38	38	39
F	31	32	33	33	34
$\frac{1}{2}$ P ₂ O ₇	20	26	33	40	46
BrO ₃	29	30	31	32	33
$\frac{1}{2}$ CO ₃	14	22	29	37	44
AsO ₂	18	18	20	21	24
IO ₃	16	17	18	18	20
$\frac{1}{2}$ B ₄ O ₇	13	13	13	13	16
$\frac{1}{2}$ B ₂ O ₄	13	14	14	15	18
$\frac{1}{2}$ S ₂ O ₅	12	12	12	12	12
$\frac{1}{2}$ SeO ₃	3	10	16	22	31

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* It may be as well to point out that the term "atomic conductivities" is rather inappropriate, and might be better replaced by "ionic conductivities."

THE ESTIMATION OF OPALESCENT SILVER CHLORIDE PRECIPITATES.*

By ROGER CLARK WELLS.

(Concluded from p. 170).

2. The Excess required to produce Maximum Opalescence.

This point has been frequently discussed. Mulder thought that four times the equivalent of soluble salt was required of the precipitant to ensure complete precipitation from silver chloride solutions. Stas considered a threefold excess sufficient. Several workers have pointed out that the earlier conclusions varied according to the means used to detect the opalescence (Hoitsema, *Zeit. Phys. Chem.*, 1896, xx., 272; Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 483). Without regard to theories, experiments were made upon this point.

KCl (N/0.000040) precipitated by AgNO₃.

Excess	5 times equivalent of KCl	Intensity of opalescence.
..	{ 31 29 }	30
" 10 "	" { 25 33 }	29
" 100 "	" "	24
" 1000 "	" "	18

Although any excess of silver nitrate up to one hundred times the equivalent of potassium chloride causes no appreciable variation of the opalescence, an excess of one thousand times causes a diminution. This may be due to the great coagulative power of ionised silver, or, more likely, to the formation of a soluble double salt.

AgNO₃ (N/0.000040) precipitated by KCl.

Excess	5 times equivalent of AgNO ₃	Intensity of opalescence.
..	{ 26 29 }	23
" 10 "	" { 24 23 30 }	26
" 50 "	" "	31
" 200 "	" "	32
" 300 "	" "	22
" 1000 "	" { 28 27 }	28

The variation of opalescence with excess is here hardly beyond the limit of error of single observations. Certainly a large excess produces no appreciable diminution of opalescence. The two preceding solutions were very concentrated in comparison with real silver chloride solutions, hence more dilute ones were next investigated.

With very dilute solutions, about N/0.000004 and small excesses, a phenomenon like supersaturation was apparent. Excesses of eight times usually failed to produce an opalescence, but excesses of ten times caused a faint opalescence. Here was illustrated the requirement that the solubility product must be exceeded before precipitation can occur. When the solubility product was barely exceeded, opalescence could be made to appear by vigorous stirring. Thus supersaturation does not appear to be limited to soluble salts, and there is no reason to suppose that it should be; but it required rather delicate regulation of the concentrations to render it visible in the case of silver chloride. The influence of the medium was very marked. Only results obtained in proper media are given below, the variations for pure water being enormous; in every case where variation with time was observed the maximum is recorded.

* From the *American Chemical Journal*, xxxv., No. 2.

KCl (N/0.0000040) precipitated by AgNO₃.

Excess	25 times equivalent of KCl ..	Opalescence.
"	75 " " KNO ₃ .. 20	9
"	75 " " HNO ₃ .. 24	24
"	75 " " Both .. 29	24
"	225 " " KCl .. {25}	30
"	450 " " KCl .. {33}	24

Here the result of too small an excess is very marked, but the diminution caused by a large excess is small, if any,

AgNO₃ (N/0.0000040) precipitated by KCl.

Excess	15-fold	KNO ₃ ..	50 minutes..	Opalescence.
"	25	"	HNO ₃ .. 40 " .. 17	14
"	25	"	KNO ₃ .. 50 " .. 18	20
"	25	"	HNO ₃ .. 4 hours .. 26	24
"	50	"	KNO ₃ .. 40 minutes.. 26	24
"	50	"	HNO ₃ .. 40 " .. 21	27
"	60	"	HNO ₃ .. 50 " .. 26	31
"	60	"	Both .. 50 " .. 27	24
"	75	"	Both .. 3 hours .. 20	18
"	100	"	KNO ₃ .. 40 minutes.. 30	24
"	100	"	HNO ₃ .. 40 " .. 30	22
"	100	"	HNO ₃ .. 2 hours .. 22	18
"	200	"	HNO ₃ .. 10 minutes..	

Notwithstanding the variations which occurred with different media and in the times at which the maxima were observed, a decided regularity is apparent. The maximum opalescence occurs with an excess of about seventy times the equivalent of the ionised silver to be precipitated. If this is more than the theory requires, it is probably due to an overcoming of the tendency towards solubility of the silver chloride in the media employed.

The phenomena for medium concentrations undoubtedly lie between the two extremes of N/0.00004 and N/0.000004 studied.

3. The Time required to obtain Maximum Opalescence.

The speed of opalescent precipitation is affected by many interrelated variables. For example, it depends upon the excess used, although the influence is not great, providing a proper excess has been used. As one would expect, the greater excess was found to cause a quicker precipitation. Silver nitrate (N/0.000004) was precipitated in two similar solutions containing nitric acid, with opalescence as follows:—

Time.	Excess 25 times.	Excess 100 times.
10 mins.	18	21
50	20	22
540	22	21

The speed is undoubtedly affected by temperature. No experiments were made to illustrate this point, since the tubes which were being compared were usually at the same temperature. The room also remained fairly constant in temperature. This question should receive attention if a method of estimation by standard glasses is perfected, so that corrections could be made for readings taken at different temperatures.

For practical purposes of nephelometry the object is to attain the maximum opalescence in the shortest time possible. The accelerating influence of certain electrolytes had been previously pointed out in a qualitative way (Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 486). It seemed wise, therefore, to study the specific influence of a number of new electrolytes, following the precipitation in a quantitative way by reference to constant glasses. Below are given some of the results so obtained.

AgNO₃ (N/0.000040) precipitated by KCl (10-fold excess).

Time.	Opalescences.								
	Without addition of any salt.	In $N/0.0025$ KNO_3 (trace of HNO_3).	$KNO_3 + HNO_3$.	HNO_3 .	Trace HNO_3 .	$Al(NO_3)_3$ (trace HNO_3).	Dilute H_2SO_4 .	Trace H_2SO_4 .	$C_2H_4O_2$.
1 min.	8	25	16	15	11	14	9	8	7
15 "	9	31	26	30	13	16	—	—	10
30 "	10	29	23	29	14	15	28	13	—
80 "	14	28	20	28	14	16	27	19	21
4 hrs.	20	24	21	26	17	16	26	24	23
14 "	21	18	18	24	16	16	23	—	24

It will be noticed that the tube containing potassium nitrate attains maximum opalescence in fifteen or twenty minutes. Next in order of speed follow the tubes containing nitric acid, potassium nitrate plus nitric acid, and sulphuric acid. The tube without any electrolyte, except that added to precipitate or that produced by metathesis, was still increasing slowly at the end of fourteen hours. The results were not always so without electrolytes, however, as was shown when considering the medium under the head "Weak Opalescences."

Such readings, extending over many hours, were made with intense, medium, and weak opalescences when precipitated by the addition of silver nitrate to potassium chloride, potassium chloride to silver nitrate, and each of these salts to actual solutions of silver chloride, in the presence of the various electrolytes above mentioned, about four hundred observations in all. The publication of these readings would require many pages. Since many of them turned out to be mere repetitions, it seems wiser to state only the general conclusions.

In general, the substances which aid in producing maximum opalescence also hasten the speed of its formation. Hence the behaviour in water alone was exceptional in every case, except that of the very weakest opalescences. No better accelerators than the "strong electrolytes," salts, and the mineral acids were found. The time of maximum opalescence with good accelerators present varied for the different cases, roughly as follows:—

Intense opalescences (about N/0.000005).

	Time of maximum.
AgNO ₃ added to KCl ..	4 minutes
AgNO ₃ added to AgCl ..	20 "
KCl added to AgNO ₃ ..	30 "
KCl added to AgCl ..	20 "

Medium opalescences (about N/0.000002).

AgNO ₃ added to KCl ..	10 minutes
AgNO ₃ added to AgCl ..	25 "
KCl added to AgNO ₃ ..	25 "
KCl added to AgCl ..	25 "

Weak opalescences (about N/0.0000005).

AgNO ₃ added to KCl ..	20 minutes
AgNO ₃ added to AgCl ..	30 "
KCl added to AgNO ₃ ..	30 "
KCl added to AgCl ..	30 "

In practice it was so difficult to control all but one variable that the results above have a relative rather than an absolute significance. Particularly, too much significance must not be attached to the times, thirty minutes and over, for the opalescence had, in those cases, become so stable that it usually varied only slightly for three or four hours further, and the exact maximum fell now at one time now at another. On this account, if the most exact results are desired, observations should always continue until opalescence begins to fade. Only in this way can one be absolutely certain that the maximum has been attained

That these insignificant variations were due to the state of the water or temperature is rendered probable by the fact that, when the maximum was late in its attainment in one case, it was late in the other tubes that day.

Perhaps the most striking fact in the results is that "actual" silver chloride solutions attain their maximum so much more uniformly than chlorides or silver salts precipitated by the opposite ion. These facts bear upon atomic weight work. In the equal opalescence method, with chloride the time of observation need not be extended beyond an hour, although no error would be introduced by so doing. In determining chloride in a silver chloride solution, however, by nephelometric methods, this point would have to be considered. The proper procedure would be to precipitate the unknown silver chloride solution, allowing it to develop for sixteen minutes, then to precipitate the standard solution, and make the comparison at the end of the next four minutes. The time would be somewhat differently adjusted if silver were being determined. But the use of a glass as a standard of reference would be the best way of all.

A small correction may now be made for this error in determining the atomic weight of sodium. Since the unknown opalescence attained its maximum after the known had begun to fade, too much standard solution was used to match, finally, the unknown opalescence; hence the soluble chloride recorded was too great. The error so committed might have amounted to 20 per cent in the solubility, therefore about 0.002 per cent in a usual determination, hence 0.001 unit in the atomic weight of sodium. The result attained by the gravimetric method, 23.006 (if $\text{Ag} = 107.93$), would become 23.007 with this correction, therefore; but the final average, with the result of the equal opalescence method, 23.009, would still remain 23.008.

It is also now very clear why, in the earlier work with the nephelometer (*Journ. Am. Chem. Soc.*, xxvii., 484), the ratio of two tubes occasionally changed enormously with time, for the standard was increasing in intensity, the unknown solution decreasing. This is shown by the following example. (Many results attained in the earlier work appeared so anomalous that they were never published).

Time.	Ratio of opalescences.
5 minutes	3.20
15 "	2.76
30 "	2.20
60 "	1.59
2.5 hours	1.19
7 "	1.08
15 "	0.99

It also becomes interesting to speculate as to the causes of the ever-shifting opalescences. It is evident that a given number of small separate visible particles will cause a greater opalescence than the same number collected into an aggregation, for the reflecting surface exposed will be greater. But if it be assumed that some of the single particles are too small to reflect light at all, that would not be true. As the latter assumption is a likely one, the development of opalescence is probably due to aggregation, and precipitation is only the point where the aggregations first attain the limit of visibility. The aggregation may be hastened initially by the presence of electrolytes. The action has been variously explained; Whetham shows agreement between the facts and the theory that a certain number of electrostatic charges must be brought within reach of a colloidal group ("A Treatise on the Theory of Solution," 1902, p. 396). Hence, he assumes that coagulation occurs in consequence of a change in the surface energy of the colloids, due to the presence of the electrostatic charge. Quincke explains the phenomena solely by surface tension changes. It seems reasonable to suppose that aggregation could only be expected to occur rapidly while the particles are small and their kinetic motion or diffusion is rapid. As aggregations become larger the pro-

cess will become slower, until a point is reached where all aggregations have attained the limit of visibility, and the exposed surface—and therefore the opalescence—begins to decrease, owing to further aggregation. The decrease is less dependent upon the medium than is the initial formation of opalescence. Moreover, a small part of the decrease is due to settling of the particles under the influence of gravity.

The above suppositions are very closely related to the present theories of colloids, and the peculiar behaviour of silver chloride has previously been ascribed to its colloidal condition (Richards and Wells, *Journ. Amer. Chem. Soc.*, xxvii., 484). But Picton and Linder have pointed out that there is probably no difference in kind between a colloid and a crystalloid (*Journ. Chem. Soc.*, 1892, lxi., 148). This is made especially clear by Beckhold in a paper upon the agglutination of bacteria (*Zeit. Phys. Chem.*, 1904, xlviii., 385). He points out that is a continuous transition from crystalloids in the first place to those bodies, partly colloidal, which aggregate in solution so as to produce high molecular weight, then to the real colloids, which look like solutions but are really suspensions, and, finally, to the visible suspensions. Many colloids are coagulated by the addition of univalent, bivalent, and trivalent salts with the relative speeds, 1:35:1023 (Schulze, *Journ. Prakt. Chem.*, 1882, xxv., 431). The action of aluminium nitrate was tried for the purpose of seeing if silver chloride belongs to this class. Since aluminium nitrate had no unusual effect, two possibilities remained. Either silver chloride is not a colloid, or else it is one which moves with an electric current, and hence, according to Hardy (*Roy. Soc. Proc.*, 1900, lxxvi., 110), one would expect only anions to affect its coagulation. Without knowing about its movement in an electric field, coagulation in the presence of sulphates was tried. These also failed to cause unusual speed of coagulation. Hence, there remained only one argument in favour of the colloid theory, the occasional colour of the opalescences. This, however, can be accounted for by strictly physical conceptions. The only tints appearing were a pale blue or a faint reddish brown; now Lord Rayleigh has shown that when the size of reflecting particles approaches the wave-length of light they begin to cease reflecting; but the short blue waves are reflected by particles small enough to transmit the red waves. It seems probable, then, that opalescences occasionally appear blue for the same reason that the sky does—the smallness of the reflecting particles. Similarly, the red tints would be accounted for by transmitted light which has lost its blue component by partial dispersion, though these were not so frequently observed as the blue tints.

It is also interesting to notice that many of the phenomena studied in this paper have a direct bearing upon photography. During the ripening of plates the change of powdery to granular silver chloride takes place. Eder records that unripe emulsions show the red and blue tints by transmitted light (*Photographie*, 1902, ix., 66). According to Liesegang the presence of potassium bromide in developers increases the size of the granules of silver (*loc. cit.*, p. 102), but this is just what would be expected in accordance with the results of the nephelometer.

4. Proper Treatment for Estimating Various Opalescences

In order to save the time of those attempting nephelometry, the precautions for several typical cases are here collected:—

Intense Opalescences (N/0.00005).

Silver nitrate added to potassium chloride: Add nitric acid or potassium nitrate. Use 8-fold excess. Read in four minutes.

Silver nitrate added to silver chloride, already containing potassium nitrate. Read in twenty minutes.

Potassium chloride added to silver nitrate: Add electrolyte. Use 50-fold excess. Read in thirty minutes.

Potassium chloride added to silver chloride, already containing potassium nitrate. Read in twenty minutes.

Weak Opalescences (N/0.000005).

Silver nitrate added to potassium chloride: Add electrolyte. Use 100-fold excess. Read in twenty minutes.

Silver nitrate added to silver chloride, already containing electrolyte. Read in thirty minutes.

Potassium chloride added to silver nitrate: Add electrolyte. Use 70-fold excess. Read in thirty minutes.

Potassium chloride added to silver chloride, already containing electrolyte. Read in thirty minutes.

In general, therefore, the object is to make the standard tubes as nearly like the unknown as possible, or, if standard glasses are being used, to attain the maximum.

The question naturally arises whether the forced maxima are really as uniform as less intense opalescences attained after repose. A considerable weight of confirmatory evidence, which will appear shortly in another paper, shows conclusively that the maxima are the best measures of the concentration. Moreover, electrolytes must be present in some solutions, and uniformity, therefore, demands that they be present in all. It is very likely that occasionally an extreme maximum will be produced, just as too weak opalescence may occur; hence the average of several observations will approach nearer the truth than only one or two.

Summary.

1. The chief sources of error in previous nephelometric work are pointed out.
2. The use of ground-glass standards of reference proved advantageous in studying the variation of opalescent precipitates with time.
3. For every concentration a suitable medium and excess of precipitant is required.
4. Electrolytes both augment the maximum opalescence to be precipitated from a solution and hasten its deposition.
5. The bearing of these facts upon other fields is pointed out.
6. Directions for procedure are given for several special cases of nephelometry.

NOTE ON "THE ESTIMATION OF OPALESCENT SILVER CHLORIDE PRECIPITATES."*

By ROGER CLARK WELLS.

In the article by me in the February number of the *American Chemical Journal* there was, I regret to state, an incorrect conclusion. In trying to estimate the magnitude of possible error upon the determination of the atomic weight of sodium due to time effects in nephelometry, I based my reasoning upon the behaviour of intense opalescences, whereas, really only weak opalescences were concerned. Prof. Richards, to whom I had, unfortunately, not presented the paper for preliminary reading, immediately called my attention to this, and I am very glad to correct it. It results therefore that the correction, if any, must be even less than 0.001 of a unit in the atomic weight of sodium, and hence quite negligible.

Let some may attach too much significance to the times of maximum opalescences, I wish to emphasise the fact that the opalescences, especially weak ones, are changing very slowly just before and after their maxima, so that the exact time to a minute means little. Moreover, the variation is occasionally large. The anomalous results illustrating this, referred to in the foot-note (p. 111, *loc. cit.*), were probably due to an insufficient excess of precipitant. Previous work had shown that a long time was often necessary for the opalescences to become relatively stable. My experiments were made to discover the means by which to obtain the maximum opalescence as speedily as possible, and showed that, under the conditions mentioned, on the average, intense opalescences become relatively stable in

from one to twenty minutes, medium opalescences in from ten to forty minutes, and weak opalescences in thirty minutes or over.

The maximum was chosen as the best measure of the opalescence, and it could always be found by comparing the opalescence at any time with an unchangeable ground glass. In consequence of the time effects above noted, such a method is more necessary for intense opalescences, which change quickly, than for weak ones which change very slowly. In the case of weak opalescences, the older procedure of waiting a long time before reading, two tubes would yield almost precisely the same result as reading each at its maximum.

In brief, then, as far as time effects in nephelometry are concerned, the time factor must be carefully regulated for intense opalescences, but it ceases to be a major variable with weak ones.—*American Chemical Journal*, xxxv., No. 6.

NOTE CONCERNING THE USE OF THE NEPHELOMETER.

By THEODORE WILLIAM RICHARDS.

A RECENT article by Dr. R. C. Wells upon "The Estimation of Opalescent Silver Chloride Precipitates" with the help of the nephelometer (*Amer. Chem. Journ.*, 1906, xxxv., 99; *CHEMICAL NEWS*, xciv. 168 *et seq.*) seems to call for a few additional remarks. The following note is written in order to supplement his suggestions, and to point out clearly the range of applicability of nephelometric methods.

Dr. Wells' conclusions are based upon a series of comparisons in which the cloudiness of a ground glass plate was used as the standard of comparison with the cloudiness produced by opalescent precipitates. This is a good idea, but it is evident that the intensity of light reflected to the eye-piece from this plate will vary with the inclination of the plate to the source of light, and therefore that great care must be taken to have this inclination always definite. Undoubtedly this was taken into account, but the necessity of this precaution was not sufficiently emphasised.

Another cause of uncertainty which, although mentioned as a possible source of error, and also heeded to some extent, may not have been quite sufficiently guarded against in the experimental work, is variation in temperature. Silver chloride is much more soluble in hot than in cold water, and the form of aggregation of the precipitate varies greatly with the temperature. Both these facts cannot but affect the rate of formation of the opalescent precipitate; hence, any work aiming at definite comparison with a fixed standard should be conducted in thermostatted tubes.

Qualitatively, it has been known for many years that the rate of decay of the opalescence, as well as the rate of precipitation, varies greatly with the "concentration" of the precipitate; in other words, with the weight of precipitate suspended in a given volume of liquid. An intense opalescence settles out much more quickly than a faint one. Dr. Wells has quantitatively estimated this difference of behaviour. A saturated solution of silver chloride, such as is usually studied by means of the nephelometer, ordinarily contains not much over 1.5 m.grms. per litre, or is only about 0.00001 N; but two-thirds of the figures given by Dr. Wells refer to solutions as strong as 0.00004 N, nearly four times as concentrated. While it is a matter of great interest to study, as Dr. Wells has done, the rapid rate of deposition of these more concentrated opalescences, they should probably not be made the basis of exact quantitative analytical work, because of their rapid rate of change. For quantitative estimation of the substance in such mixtures, it is better not to use the nephelometer, but to collect the precipitate after it has been wholly deposited. The nephelometer should be employed for exact work only

* See *CHEMICAL NEWS*, vol. xciv., p. 168 *et seq.*

when the precipitate is so finely divided that it will not in any reasonable time, for example, two or three days, deposit itself and thus place itself within the range of ordinary quantitative determination.

It should be strongly emphasised that the "anomalous results" mentioned by Dr. Wells has been duly considered in previous work, and were distinctly pointed out, but the bulk of the previous papers was concerned with indicating the way in which the difficulties can be overcome; therefore but few figures were given.

While the ground glass plate employed by Dr. Wells, when properly and steadily illuminated, undoubtedly affords an excellent means of studying the rate of change in a given mixture, I cannot believe that it provides the best standard of reference for analytical purposes, because it is unaffected by the many variables which affect the mixture to be estimated. In my opinion, if even moderately accurate analytical results are to be had with the nephelometer, the one essential point to be heeded is this:—*The unknown solutions to be estimated must be treated in exactly the same way as the known standard solutions, which serve as the basis of comparison.* If this precaution is adhered to, the changes of temperature, the presence of electrolytes, the concentration of the solutions and all the other variables, affecting each precipitate in like manner, are eliminated from the comparison. This method, indeed, is a fundamental principle in all precise volumetric analysis.

That this precaution was realised in the previous discussion of the instrument may be shown by the following quotation:—

"Care must be taken to have both standard solution and unknown solution subjected to precisely the same conditions, for varying conditions of precipitation may lead to differences in the appearance of the precipitate far greater than the possible optical error of the apparatus. Herein lies the chief caution to be noted in its use.

"The contents of this paper may be summarised as follows:— . . . The chief possibility of error lies in the state of the precipitated material. In order to exclude variation here, the solution to be estimated and the standard solution for comparison should be precipitated in exactly the same way." (Richards and Wells, *Amer. Chem. Journ.*, 1904, xxxi., 242; it should be noted that both these sentences were written by the author, who takes all the responsibility attached to them).

On the same page with these statements is to be found a series of results showing, positively, that when this advice is heeded, and when sufficient time is allowed for the opalescence to develop, the instrument gives reasonably accurate results, and similar evidence is given in another place.

In the course of the work upon the atomic weight of sodium, a singular anomaly was observed, namely, the fact that the opalescence of silver chloride forms more quickly when a solution of this salt is treated with a large excess of silver nitrate than it does when an equivalent solution of sodium chloride is treated in the same way. This irregularity leads to an uncertainty as to whether the weights of precipitate corresponding to a given maximum intensity of opalescence are equal in the two cases—an uncertainty clearly pointed out in the place mentioned. The question of weight is not discussed in Dr. Wells' paper, but is now being exhaustively studied at Harvard. The uncertainty arose only because of a slight infringement of the rule italicised above. When the two mixtures are subjected to the same conditions—for example, when both are re-dissolved in ammonia and re-precipitated, the uncertainty disappears. This practice is being adopted in a research on the atomic weight of potassium, now being pursued at Harvard by Dr. A. Stähler, of Berlin, and the author.

In brief, the object of this note may be summarised as follows:—It is pointed out that, while the recent paper of Dr. R. C. Wells on the nephelometer affords interesting data concerning the rate of precipitation of opalescent

precipitates, particularly in cases verging upon prompt deposition, it does not emphasise the chief precaution which, in the authors' opinion, should be adopted if the nephelometer is to be used in quantitative analytical work.—*American Chemical Journal*, xxxv., No. 6.

ON THE COMPOSITION OF PETROLEUM.*

THE SULPHUR COMPOUNDS AND UNSATURATED HYDROCARBONS IN CANADIAN PETROLEUM.†

By CHARLES F. MABERY and WILLIAM O. QUAYLE.

In a paper published some time ago by one of us on a preliminary examination of Canadian petroleum (Mabery, *Amer. Chem. Journ.*, 1891, xlii., 89), it was stated that 225 litres of sulphur oil from Canadian burning oil was in process of distillation for the purpose of separating the individual sulphur constituents. On account of the pressure of other lines of work, study of those distillates was delayed, but it has been resumed at intervals until the results described in this paper were obtained.

On returning to this work it seemed worth while to ascertain first whether the oil selected really represented constituents of crude petroleum, or whether it consisted, to a greater or less extent, of decomposition products incident to the process of refining. Since the question of decomposition could be determined in sulphur petroleum from any source, a quantity of crude oil from the Lima, Ohio, field was distilled *in vacuo*, and the distillate, corresponding to that from which burning oil is prepared, carefully separated and agitated thoroughly with alcoholic mercuric chloride, for the purpose of precipitating the sulphur compounds. The oil was next agitated vigorously with ordinary sulphuric acid, the acid sludge drawn off, and diluted with water, carefully avoiding heat so far as possible.

As usual, a dark red oil separated above the solution, but it lacked the heavy sulphurous odour characteristic of sludge as it is ordinarily separated from sulphur petroleum. The odour of this oil resembled that of sludge after the sulphur compounds had been removed, and it showed still greater similarity in its behaviour toward bromine, with which it readily united with the evolution of heat, and the formation of an addition product heavier than water, precisely similar to the behaviour of sludge products. The precipitate with mercuric chloride resembled, in all respects, the characteristic products which are so useful in separating the sulphur compounds.

As further evidence of the presence of unsaturated hydrocarbons in this oil, a portion of the oil precipitated from sulphuric acid was heated with concentrated hydrobromic acid to 100°, and the product fractionated *in vacuo* to collect, in a smaller limit, the bromine addition product. It was not intended to prepare an individual bromine derivative sufficient for analysis, since this would have been impossible with the small amount to be obtained in this manner, but only to be sure that an addition product with hydrobromic acid could be formed. The higher vacuum distillate gave an abundant reaction for bromine after heating with lime, showing that addition of the acid had taken place. The results of these experiments are described in full, that there may be no misapprehension concerning the source of the sulphur compounds and unsaturated hydrocarbons which will be described in this paper. They confirm the results of similar experiments described in the former paper.

In continuing the distillation of the 225 litres of crude sulphur oil, with the aid of the apparatus elsewhere

* Contributions from the Chemical Laboratory of Case School of Applied Science. From the *American Chemical Journal*, xxxv., No. 5.

† The sulphur derivatives of the hydrocarbons described in this paper are evidently members of a new series, differing essentially in composition, physical properties, and chemical relations from any of the well-known series of sulphur compounds. For this new series I suggest the name Thiophane.—C. F. M.

described, the distillates were carried through entire up to 230° (50 m.m.) at first within 5°, during four distillations. The lower fractions were then continued within single degree fractions until the lower portions could be distilled under atmospheric pressure. It was not possible to accomplish in this manner more than a general separation, since all the distillates were mixtures, yet the value of the great amount of tedious labour was shown after the separation of the individual constituents, of which the greater portion distilled at approximately the same temperatures as the original distillates; and although it seemed a great expenditure of effort to distil such a large volume of oil in quantities of 10 litres, the capacity of the porcelain still employed, and to continue the distillation of the entire quantity, this seemed to be the only available method for the separation of these peculiar bodies from the crude oil. When first collected, all the fractions were nearly colourless, but on standing they turned dark red, especially those with higher boiling-points. The fractions collected below 125° (50 m.m.) were found to be exceedingly unstable. On standing from six months to two years, some of these distillates deposited very dark, heavy oils, doubtless formed from unstable unsaturated hydrocarbons, terpenes, or sulphur compounds by polymerisation.

In separating the constituents of the vacuum distillates, we followed, in general, the method described in a former paper. 300 or 400 grms. of the oil were shaken in a large flask with an excess of an alcoholic solution of mercuric chloride, which gave a heavy precipitate, crystalline in the lower fractions, a thick viscous mass in the less volatile, and a heavy oily deposit in the vacuum distillates above 160°. There invariably separated above the alcohol a lighter oil, which contained no sulphur, or at most, analysis showed less than 0.5 per cent. Upon diluting the alcohol more lighter oil collected, which doubtless has a different composition from the other, since, as will appear later, it showed essentially different properties.

In recovering the sulphur compounds from the mercuric chloride precipitates, after thoroughly washing with alcohol and very volatile gasoline, the precipitate was decomposed by hydrogen sulphide, in presence of a considerable volume of alcohol, the mercuric sulphide separated by filtration, washed with alcohol, and the alcohol largely diluted. For the most part the lighter oil separated, some remaining in suspension, which collected after standing a short time. With all possible care in washing the mercuric chloride precipitate, a single precipitation was never sufficient to remove all the sulphur-free oil. The percentages of sulphur in the individual sulphur compounds invariably came from 1 to 3 per cent too low, however long they were fractionated, until they were a second time converted into the mercuric chloride compound and again separated by hydrogen sulphide. Upon diluting a second time, usually another portion of the sulphur-free oil collected, or remained in suspension, and, after sufficient fractioning, the percentage of sulphur then corresponded to the value theoretically required.

It has already been explained that the vacuum fractions of the crude sulphur oil, before the separation of its constituents, is a mixture of an unsaturated hydrocarbon, a sulphur compound, and another hydrocarbon of a series not determined. More attention will be given later to the sulphur-free oils. All the portions selected for the separation of these constituents had previously been fractionated from four to twenty times, for the most part *in vacuo*, and since the sulphur oil from any particular fraction has corresponded in boiling-point to that of the fraction before separation, it has been possible to select, from the great number of first fractions, those which should give the bodies desired, thereby saving much time and unnecessary labour in searching for the individual constituents.

After the second precipitation from the mercuric chloride compound, a few distillations *in vacuo*, with the aid of a bead column, in a long-necked flask, have been sufficient to bring together, for the most part within 1° or 2°, the sulphur compound desired. For the separation without

decomposition of the sulphur oils boiling above 130°, distillation *in vacuo* has been indispensable. Doubtless exclusion of air, as well as the reduction in boiling-points, especially of the higher members, is essential.

The most volatile vacuum distillates, 40—50°, were subjected to eight additional distillations within limits of 2°, and 300 c.c. of these distillates was agitated with an excess of alcoholic mercuric chloride. A part of the oil was immediately converted into a crystalline precipitate, and the sulphur-free oil, which formed the greater part of the oil taken, remained entirely in solution, and was separated by dilution. After decantation of the alcoholic solution, the crystalline precipitate was well washed with alcohol and light gasoline, and decomposed by hydrogen sulphide in presence of alcohol.

For complete removal of the sulphur-free oil the mercuric chloride compound was again formed, washed, and the sulphur oil separated by hydrogen sulphide. Unfortunately, the larger portion of the sulphur oil was accidentally lost, but the remainder was fractionated, so far as possible, until, finally, it showed a tendency to collect at 125—130°.

The percentage of sulphur found in this product was 27.12; required for the sulphur compound, $C_6H_{12}S$, 27.60°. The crystalline condition of this substance is characteristic of the alkyl sulphides; but all the sulphur bodies we have separated from petroleum are viscous oils that could not be solidified, except the more volatile sulphur compounds such as were separated from Ohio petroleum, which were crystalline.

The following series of sulphur compounds, which have been identified by analysis and shown to have the composition of the general formula $C_nH_{2n}S$, do not represent any series known. They are not members of the ethylene sulphide series, as shown by their reactions and very high specific gravity. In empirical composition they correspond to hydrothiophenes, which have not been synthetically prepared.

Heptyl Thiophane.

(Fraction 158—160°, $C_7H_{14}S$).

The heptyl sulphur compound was identified in the vacuum distillate 71—73° (50 m.m.) seventh distillation. After precipitation with alcohol mercuric chloride, and thorough washing with alcohol and light gasoline, the thick viscous oil was decomposed with hydrogen sulphide, in the presence of alcohol. The oil that separated on dilution of the alcohol was fractionated *in vacuo* until it distilled at 74—76° (50 m.m.) and at 158—160° (750 m.m.). A determination of its sp. gr. at 20° gave 0.8878. Analysis gave percentages of carbon, hydrogen, and sulphur required for the formula $C_7H_{14}S$. Carbon and hydrogen were determined by combustion in lead chromate, the sulphur by combustion in oxygen.

I. 0.1749 grm. oil gave 0.4141 grm. CO_2 and 0.1748 grm. H_2O .

II. 0.1666 grm. oil gave 0.3071 grm. BaO_4 .

	Calculated for $C_7H_{14}S$.	Found.	
		I.	II.
C	64.63	64.59	—
H	10.76	11.18	—
S	24.61	—	25.31

Octyl Thiophane.

(Fraction 167—169°, $C_8H_{16}S$).

For the separation of the next sulphur homologue the large quantity of distillate was selected that collected at 79—81° (50 m.m.) after the seventh distillation. 100 c.c., with the treatment described above, yielded 20 c.c. of the sulphur compound that distilled constant at 81—83° (50 m.m.), and at 167—169° under atmospheric pressure. The sp. gr. of this oil was found to be 0.8929 at 20°. Analysis:—

I. 0.1666 grm. oil gave 0.4057 grm. CO_2 and 0.1671 grm. H_2O .

II. 0.1391 grm. oil gave 0.2282 grm. $BaSO_4$.

	Calculated for $C_8H_{16}S$.	Found.	
		I.	II.
C	66.67	66.46	—
H	11.11	11.22	—
S	22.22	—	22.53

Isocetyl Thiophane.
(Fraction 183—185°, $C_8H_{16}S$).

A large amount of distillate collected at 97—99° (50 m.m.), at the end of the seventh distillation, that gave, by analysis, the same empirical formula as the sulphur compound previously described. The term isocetyl is applied to this compound to distinguish it from its isomer. Upon treatment with mercuric chloride and second precipitation, a large amount of sulphur-free oil collected on dilution of the alcohol, and analysis showed that this constituent was completely removed by the second treatment. After fractionating *in vacuo* this product collected to the extent of 15 c.c. at 94—96° (50 m.m.), and distilled with some decomposition at 183—185°, atmospheric pressure. Sp. gr. at 20°, 0.8937. Analyses:—

- I. 0.1458 grm. oil gave 0.3592 grm. CO_2 and 0.1470 grm. H_2O .
 II. 0.1561 grm. oil gave 0.3814 grm. CO_2 and 0.1575 grm. H_2O .
 III. 0.2670 grm. oil gave 0.4183 grm. $BaSO_4$.

	Calculated for $C_8H_{16}S$.	Found.		
		I.	II.	III.
C	66.67	67.19	66.16	—
H	11.11	11.27	11.29	—
S	22.22	—	—	21.52

It will be observed that the last two compounds have the same empirical composition, but differ by 16° or more in boiling-points, and differ also in specific gravity. It will also be observed that they agree closely in boiling-points with butyl and isobutyl sulphides; but they differ widely from the latter in specific gravity:—Butyl sulphide, 0.8523 at 0°; isobutyl sulphide, 0.8363 at 10°; and in other properties.

Nonyl Thiophane.
(Fraction 139—195°, $C_9H_{18}S$).

A portion of the distillate that collected in considerable quantity at 106—108° (50 m.m.) was treated in the same manner as previously described, with two precipitations for the separation of the sulphur compound. The product was fractionated *in vacuo* until it collected, for the most part, at 106—108° (50 m.m.). Under atmospheric pressure it boiled at 193—195°, and gave, as its sp. gr. at 20°, 0.8997. Analyses:—

- I. 0.1927 grm. oil gave 0.4852 grm. CO_2 and 0.2033 grm. H_2O .
 II. 0.1547 grm. oil gave 0.2210 grm. $BaSO_4$.

	Calculated for $C_9H_{18}S$.	Found.	
		I.	II.
C	68.35	68.68	—
H	11.40	11.80	—
S	20.25	—	19.62

Decyl Thiophane.
(Fraction 207—209°, $C_{10}H_{20}S$).

From the vacuum distillate, 114—115° (50 m.m.) after the seventh distillation, a sulphur oil was prepared by two precipitations with mercuric chloride that collected, after fractionating some time *in vacuo*, for the most part at 114—116° (50 m.m.). It distilled at 207—209° (750 m.m.) and gave sp. gr., at 20°, 0.9074. Analyses:—

- I. 0.2323 grm. oil gave 0.5904 grm. CO_2 and 0.2453 grm. H_2O .
 II. 0.1981 grm. oil gave 0.5078 grm. CO_2 and 0.2094 grm. H_2O .
 III. 0.1654 grm. oil gave 0.2240 grm. $BaSO_4$.
 IV. 0.1760 grm. oil gave 0.2407 grm. $BaSO_4$.

	Calculated for $C_{10}H_{20}S$.	Found.			
		I.	II.	III.	IV.
C	69.77	69.33	69.92	—	—
H	11.62	11.32	11.82	—	—
S	18.60	—	—	18.59	18.78

Undecyl Thiophane.
(Fraction 128—130° (50 m.m.), $C_{11}H_{22}S$).

The vacuum distillate, 135—145° (50 m.m.), was selected for the separation of the next homologous sulphur compound. A thick tarry mass was formed by precipitation with mercuric chloride, which gave the pure sulphur oil by a second precipitation. The viscosity of the compounds with mercuric chloride was found to increase with increase in molecular weights of the sulphur oils. 300 grms. of the first distillate, 135—145°, fourth distillation, gave, after the second precipitation with mercuric chloride, 122 grms. insoluble in alcohol, 60 grms. in the alcoholic solution, and 84 grms. of the sulphur oil. Without further purification, the latter gave 16.08 per cent sulphur. After continued fractioning *in vacuo* the sulphur oil collected for the most part at 128—130° (50 m.m.). Analyses:—

- I. 0.1793 grm. oil gave 0.4669 grm. CO_2 and 0.1896 grm. H_2O .
 II. 0.2064 grm. oil gave 0.5334 grm. CO_2 and 0.2122 grm. H_2O .
 III. 0.1921 grm. oil gave 0.2411 grm. $BaSO_4$.

	Calculated for $C_{11}H_{22}S$.	Found.		
		I.	II.	III.
C	70.98	71.01	70.71	—
H	11.82	11.82	11.50	—
S	17.20	—	—	17.24

The sp. gr. of this sulphur oil was found to be 0.9147 at 20°. Particular attention was given to the purification of this product, to be certain of the series as shown by the most careful analysis. In addition to the determinations given above that demonstrate its composition, the following additional analyses were made of different preparations:—Carbon found, 70.73, 70.74; hydrogen in the same combustions, 11.48, 11.95; sulphur, 17.28, 17.05, 17.10.

The portions of the original sludge oil, called sulphur-free oils to distinguish them from the sulphur oils, have contained from 0.1 to 0.3 per cent of sulphur, and it has been assumed that the small proportion of sulphur indicated a little of the sulphur compound not precipitated by mercuric chloride. That the part collecting above the alcohol, after precipitation, is a different product from the part remaining in solution in alcohol is shown by the difference in specific gravity. For example, the distillate 136—145°, from which the oil $C_{11}H_{22}S$ was obtained, gave an oil insoluble in alcohol with sp. gr. 0.8412; but the sp. gr. of the portion in solution was found to be 0.8107. Similar differences appeared in oils associated with other thiophanes. Since the specific gravity of any one of the principal hydrocarbons in Canadian petroleum corresponding in boiling-point with these bodies is smaller than the specific gravity of the sulphur oils, and since hydrocarbons are sparingly soluble in sulphuric acid and alcohol, the bodies under examination cannot be the principal petroleum hydrocarbons. Then the odours of both the substances soluble and insoluble in alcohol are unlike that of any of the hydrocarbons—very pungent, resembling the terpenes. Further study will be necessary to identify these peculiar bodies.

Quatdecyl Thiophane.
(Fraction 266—268°, $C_{14}H_{28}S$).

This sulphur oil was separated from the distillate 160—170° (50 m.m.), fourth distillation. After the second precipitation and decomposition by hydrogen sulphide, 400 grms. of the sludge distillate gave 75 c.c. of a yellow oil that collected, for the greater part, at 168—170° (50 m.m.), after extended fractioning. It collected at 266—268°

(750 m.m.) Its sp. gr. at 20° was found to be 0.9208. Analyses:—

- I. 0.1859 grm. oil gave 0.5010 grm. CO₂ and 0.2109 grm. H₂O.
II. 0.2290 grm. oil gave 0.2336 grm. BaSO₄.

	Calculated for C ₁₄ H ₂₈ S.	Found.	
		I.	II.
C	73.68	73.52	—
H	12.28	12.69	—
S	14.04	—	14.02

Sexdecyl Thiophane.
(Fraction 283—285°, C₁₆H₃₂S).

From 400 c.c. of the first vacuum distillate 170—180° (50 m.m.), after the second precipitation with mercuric chloride and long-continued distillation, 28.5 grms. of the sulphur oil collected at 184—186°, which distilled, with some decomposition, at 283—285° (750 m.m.). Its sp. gr. was found to be 0.9222. Analyses:—

- I. 0.2148 grm. oil gave 0.5934 grm. CO₂ and 0.2380 grm. H₂O.
II. 0.1850 grm. oil gave 0.1683 grm. BaSO₄.

	Calculated for C ₁₆ H ₃₂ S.	Found.	
		I.	II.
C	75.00	75.36	—
H	12.50	12.40	—
S	12.50	—	12.49

To be continued).

NOTICES OF BOOKS.

A Text-book of Sanitary and Applied Chemistry. By E. H. S. BAILEY, Ph.D. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1906.

THE chief value of this book lies in the excellent descriptions of experimental work which are given at intervals throughout the text, and which should add greatly to the students' interest in the subject. Although the book is in some respects superficial, and attempts to cover a very wide area, it will at any rate be found stimulating by those who wish to get some idea of the chemistry of daily life, and it gives a very readable account of foods in particular; the notes on economy in the preparation of foods, for example, are thoroughly sensible and practical, and the experiments to illustrate the properties and uses of different classes of food substances are well chosen and clearly described. The chapters devoted to sanitary chemistry deal with the atmosphere, and methods of detecting and removing impurities, fuels, and lighting from the economic point of view, water, sewage and its disposal, and the use of cleaning materials and disinfectants. From this enumeration of the contents of the chapters it will be seen that completeness has been the author's aim more than the exhaustive treatment of any one subject, but the book contains a wonderful amount of useful information compressed into a comparatively short volume, and in the hands of a teacher who, basing his lectures upon the experiments in the book, supplements and enlarges, it should be a valuable aid to the teaching of sanitary and applied chemistry.

Technical Thermometry. List No. 39, The Cambridge Scientific Instrument Co., Ltd. Cambridge: The University Press. 1906.

LIST No. 39 of the Cambridge Scientific Instrument Company is far more than a mere catalogue of apparatus, and is well worth the attention of all who are interested in the measurement of temperature. The various appliances are

classified according as they are intended more particularly for commercial purposes, or for research and more delicate scientific work. In the first class are included electrical resistance thermometers, which are listed at various prices according to construction and outfit, and thermo-electric thermometers, among which is described a very interesting and novel recording instrument, called a Thread Recorder, which is said to be exceedingly sensitive, and certainly seems from the description to be most simple and convenient. Féry radiation pyrometers are also illustrated in this section, while in the second part the similar but more accurate and delicate measuring instruments, bridges, galvanometers, &c., which are essential if a high degree of accuracy is aimed at, are catalogued. A short appendix which concludes the list deals with theoretical considerations, and contains some tables of general interest.

Das Erdöl und Seine Verwandten. ("Petroleum and its Allies"). By HANS HÖFER. Second Edition. Braunschweig: Friedrich Vieweg und Sohn. 1906.

THE second edition of this book follows the plan of the first, which was one of the earliest of German treatises to treat the subject of petroleum in a thoroughly scientific manner, and the value of which was so universally recognised that it was widely used, and was translated into English. Since its first appearance other books dealing with petroleum, more especially from a geological point of view, have been published, but the great advances which have recently been made in our knowledge make this second edition very welcome. It has been subjected to a careful revision, and much new matter has been added, so that the book has greatly increased in size and correspondingly in value. The statistical information has been brought down to the present day, and the various modern theories put forward as to the origin of petroleum are discussed very fully. As in the earlier edition, the methods of obtaining the oil are treated only very shortly, the chief aim of the author being to provide a thoroughly scientific treatise on the natural history of petroleum and its allies.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 11, September 10, 1906.

Atomic Weight of Silver.—Ph. A. Guye and G. Ter. Gazarian.—The authors make a series of researches on the atomic weight of silver, as there has hitherto been some discrepancy in the numbers obtained. Their experiments are chiefly directed towards the determination of the causes of error in the former investigations. They find that the chief error lies in the fact that the chlorate of potash always contains traces of chloride, and the presence of one ten-thousandth of chloride in the KClO₃ raises the atomic weight of silver by 0.0177. The mean of the two best applications of the method of the halogenates, corrected and completed as the authors describe, is the number 107.893, or, in round numbers, 107.89. The mean value of ten analyses, all of different silver salts, give as a mean 107.890, and the results are so remarkably concordant that the authors assert that the atomic weight of silver should be lowered from 107.93 to 107.89. This alteration would entail a corresponding correction in a large number of other atomic weights.

MISCELLANEOUS.

Appointment.—Mr. Geo. Clarke, F.I.C., Head of the Chemical and Agricultural Department, County Technical Laboratories, Chelmsford, has been appointed on the staff of the Indian Agricultural Service by the Secretary of State for India in Council. Mr. Clarke studied at Nottingham University College, 1897-1901, and was afterwards a Demonstrator in the Chemical Department of the School of Technology, Manchester. He succeeded Mr. T. S. Dymond at the Chelmsford Laboratories in 1904.

MEETINGS FOR THE WEEK.

WEDNESDAY, 17th.—Microscopical, 8. "Some Rotifera of the Sikkim Himalaya," by J. Murray. "*Cornuvia serpula*—a species of Mycetozoa New to Britain," by J. M. Coon.

THURSDAY, 18th.—Chemical, 8.30. Presentation of Longstaff Medal to Prof. W. N. Hartley. "The Aminodicarboxylic Acid derived from Pinene," by W. A. Tilden and D. F. Blyther. "Preparation and Properties of Dihydropinylamine (Pinocampylamine)," by W. A. Tilden and F. G. Shephard. "Determination of Nitrates," by F. S. Sinnatt. "Nature of Ammoniacal Copper Solutions," by H. M. Dawson. "Malacone—a Silicate of Zirconium containing Argon and Helium," by S. Kitchen and W. G. Winterson. "Relationship of Colour and Fluorescence to Constitution—Part I., Condensation Products of Mellic and Pyromellitic Acids with Resorcinol," by O. Silberrad. "Colouring-matters of the Stilbene Group" (Part III.), by A. G. Green and P. F. Crossland. "Separation of α - and $\beta\beta$ -Dimethyladipic Acids" and "Action of Alcoholic Potassium Hydroxide on 3-Bromo-1:1-dimethylhexahydrobenzene," by A. W. Crossley and N. Renouf. "Compounds of Pyridine with Dichromates" and "Normal Chromates and the Unsaturated Character of the Chromate Radical," by S. H. C. Briggs. "Interaction of Succinic Acid and Potassium Dichromate—Note on a Black Modification of Chromium Sesquioxide" and "Derivatives of Polyvalent Iodine—The Action of Chlorine on Organic Iodo-derivatives, including the Sulphonium and Tetra-substituted Ammonium Iodides," by E. A. Werner. "New Derivatives of Diphenol (4:4'-Dihydroxydiphenyl)" and "The so-called 'Benzidine Chromate' and Allied Substances," by J. Moir. "Interaction of the Alkyl Sulphates with the Nitrites of the Alkali Metals and Metals of the Alkaline Earths," by P. C. Ray and P. Neogi.

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PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	V. H. BLACKMAN, M.A.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
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VOL. XCIV., No. 2447.

NEW LOW TEMPERATURE PHENOMENA.*

By Prof. Sir JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S.

(Concluded from p. 175).

Separation of Highly Concentrated Oxygen from Air by Charcoal at Low Temperatures.

In order to examine the changes taking place in a mixed gas like air during the absorption, a quantity of about 50 grms. of charcoal was after heating and absorption saturated at -185° in a current of pure dry air—got by passing the air current through a U-tube immersed in liquid air.

For a time the air rushed into the charcoal with great rapidity, and in about ten minutes between 5 and 6 litres were taken in. A manometer attached to the vessel containing the charcoal showed, on shutting off the air current, that during the early part of the saturation the absorption was so effective as to give practically no measurable mercury pressure. As soon as the absorption was ended, and a current began to pass slowly over the charcoal, the composition of the air leaving the charcoal showed 98 per cent nitrogen. After the current of air had passed for half-an-hour, the total gas occluded in the charcoal was expelled by taking the vessel in which it had been treated out of the liquid air, and allowing the temperature to rise to 15° C.

The gas, which was rapidly expelled, measured 5.7 litres, and contained 56 per cent of oxygen. If the saturated charcoal before heating was subjected for an hour to the action of an air-pump, capable of giving a steady exhaustion of 5 m.m., no difference was effected in the oxygen percentage of the evolved gas. The same experiment was repeated with this variation, that, instead of the air current having the pressure of the atmosphere, it was kept below one-tenth of an atmosphere. In this experiment 4.8 litres were expelled on heating up, and the percentage of oxygen was 58. Then a further repetition was made with an air current supplied at a pressure not exceeding 5 m.m. of mercury. After three hours' treatment, the charcoal, on heating to 15° C., gave 4.4 litres of 57 per cent oxygen. From these experiments it follows that the tension of the occluded gases, at the temperature of liquid air, must be very small, and thus the use of low temperatures, combined with charcoal, introduces a new and greatly improved means of getting high vacua, which in the future may be found susceptible of important practical applications. These experiments are quite conclusive as to the practical constancy of the mean composition of the air, gases occluded in the charcoal (subject to the conditions aforesaid), and they further show that wide changes in the pressure of the air current has little or no effect in altering the proportions. In another experiment, the vessel containing the saturated charcoal, instead of being allowed to rise rapidly in temperature, was transferred to a vacuum vessel, in which a little liquid air was placed, in order that the temperature might rise slowly, and thereby enable the successive litres of gas given off to be collected separately, and analysed.

This experiment gave the following results:—

	Oxygen per cent.
First litre	18.5
Second „	20.6
Third „	53.0
Fourth „	72.0
Fifth „	79.0
Sixth „	84.0

The mean composition of the 6 litres is again 56 per cent oxygen. From the above experiments it follows that one of the most rapid means of extracting a high percentage of oxygen from atmospheric air is to absorb it in charcoal at low temperatures, and thus to expel it either rapidly or slowly by heating the mass of charcoal to the ordinary temperature.

A few experiments have been made using, instead of air, special mixtures of oxygen and nitrogen. Thus it was found that a gas containing 6.5 per cent of oxygen, used in the same manner as in the air occlusion experiments, gave, on heating up the charcoal rapidly to 15° C., 5 litres of gas having the composition of 23 per cent of oxygen. A repetition of the same process with the 23 per cent of oxygen would have raised the percentage about 60 per cent, or a stronger concentration could have been reached by fractionating the gas as it slowly leaves the charcoal on gradually increasing the temperature.

Production of High Vacua and Spectroscopic Studies. Separation of Gases like Helium, Neon, and Hydrogen from Air and other Gas Mixtures (Roy. Soc. Proc., 1904).

The high absorption of gases by charcoal suggested an inquiry into the limits of gaseous pressure reached by such means of condensation. With this object, an ordinary spectroscopic sparking tube, A B, was sealed to a narrow tube, C D, the end of which was blown into a bulb, D E, capable of containing a few grms. of cocoanut charcoal. After the charcoal had been freed from gases by heating and exhaustion, and the poles cleared by sparking during this operation, pure and dry gases like oxygen, nitrogen, air, carbonic oxide, hydrogen, neon, and helium, could be admitted at different pressures, and the tube with its attached charcoal chamber sealed off.

On placing the charcoal capsule in liquid air, gas in each case was rapidly absorbed and the vacuum produced reached the phosphorescent stage, except in the cases of hydrogen, neon, and helium.

A large spectroscopic tube of 1300 c.c. capacity was sealed to a bulb containing 30 grms. of charcoal. When the tube was filled with air at atmospheric pressure and the charcoal cooled in liquid air, the pressure fell to 50 m.m. of mercury. On re-filling the tube with air at the pressure of half an atmosphere, and treating it as before, the exhaustion reached beyond the striæ stage, and a final charge at a quarter of an atmosphere gave a vacuum through which no spark passed. When the experiment was repeated with only 1 gm. of charcoal, and an initial pressure of 3 m.m. of mercury, the vacuum just reached the beginning of the phosphorescent stage.

When hydrogen was employed, in order to get a vacuum well up in the striæ stage, either a larger amount of charcoal had to be employed or the initial pressure had to be less than an atmosphere. But if the liquid air-bath was cooled to -210° C. by exhaustion, the tube just reached the beginning of phosphorescence round the cathodes. With helium there was very slight absorption, but more appreciable results were obtained with neon. Spectroscopic observations made during the condensation of the gas in the charcoal showed the gradual disappearance of the characteristic spectrum of oxygen, nitrogen, and air, as the high vacuum was reached, and the discharge passed with great difficulty. In tubes of this kind filled at atmospheric pressure, the F line of hydrogen and the neon yellow could always be seen; but the helium was not seen with any definiteness. As the amount of neon in the air cannot well exceed 1/50,000th, the spectroscopic test is very delicate.



FIG. 2.

* A Discourse delivered at the Royal Institution, January 20, 1905.

In order to get the helium spectrum the air in the sparking tube had to be enriched six or seven times. This was attained by the apparatus in Fig. 3. *AB* is the sparking tube, with its small charcoal bulb, *C*, attached, capable of being sealed off at *G* when required; and *D* and *E* are larger charcoal absorbers placed in vacuum tubes containing liquid air; the whole being attached to a graduated gas-holder, *F*, containing air. A series of glass stopcocks are attached at the points *H*, *I*, *J*, and *K*, to facilitate manipulation.

In a preliminary experiment to determine the volume of air necessary to bring in the helium lines, 200 c.c. of air were supplied to one of the charcoal vessels, *D*, containing 15 grms. of charcoal, from which the residue was passed on to the sparking tube. This tube gave the hydrogen lines *C* and *F*, the neon yellow, and some of the orange lines, along with the helium yellow and green quite distinctly. Another tube with the residuary gas from a litre of air gave all the helium lines as well as the neon yellow and the hydrogen *F*; from which we infer that by this means 1/50,000th of helium can be detected, so that the test is as delicate for helium as for neon. A third tube, supplied from 3 litres of air, gave the neon and helium spectra and a brilliant ruddy glow discharge.

As 40 to 50 grms. of charcoal can absorb at the temperature of liquid air from 5 to 6 litres of air, it is easy to

may be treated by the charcoal method. As an example, I have applied this method to the crude gases got by heating the mineral Fergusonite. During the cooling of the charcoal the nitrogen and hydrogen spectra were marked, but in a short time nothing could be seen but the lines of hydrogen and helium. It is needless to say that the charcoal method of exhaustion can be applied to the manufacture of incandescent lamps and Röntgen radiation tubes, and that the method can be conveniently employed to produce and maintain high vacuum for the purpose of distilling bodies under low pressures. Many experiments with the radiometer can be carried out by the use of the charcoal method of exhaustion. If a charcoal capsule is sealed to the bulb of a radiometer full of air under relatively high pressure, on directing a beam of light on the vanes of the radiometer they remain at rest, showing that the density of the air is too great for motion to take place. When, however, the charcoal capsule is immersed in a vessel containing liquid air, the vanes immediately commence a rapid rotation. On removing this liquid air-bath their motion slackens, and, finally, they come to rest as the charcoal returns to the temperature of the room.

It is known that dry phosphorus does not enter into chemical combination with pure oxygen at ordinary temperature and pressure. A bulb of from 100 to 200 c.c. filled with pure oxygen, having a side tube sealed on of 2 m.m.

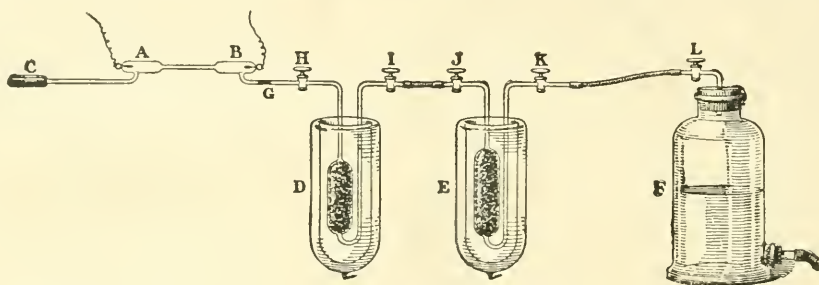


Fig. 3.

accumulate rapidly the uncondensed gases in considerable quantities for spectroscopic examination. For this purpose it is convenient to use two charcoal condensers in circuit. After the charcoal in the first one, marked *E* in figure, was saturated, the stopcock, *K*, was closed, while *I* and *J* were opened for a short time to allow the less condensable gas in *E* to be sucked into the second condenser, *D*, along with some portion of air. The condenser, *E*, was then taken out of the liquid air, rapidly heated to 15° C. to expel the excluded air, and was thus ready to repeat the operation. In this way 50 litres of air can be treated in a short time, supplying sparking tubes showing brilliantly the complete spectra of the volatile constituents of the air.

The results derived from the treatment of Bath gas in this way are interesting. This gas, consisting mainly of nitrogen and 1/1000th part helium, when subjected to the action of the charcoal condenser in liquid air, gives no high vacuum. All the nitrogen and any other constituents are absorbed, and a spectrum of helium and hydrogen showing much less neon than exists in the volatile residue from atmospheric air is the result. A sample of argon prepared from Bath gas treated in the same way, gives a tube showing the helium and neon spectrum; and one prepared from atmospheric air gives a similar result, but the helium spectrum is the stronger in the Bath argon, whereas with the atmospheric argon the neon spectrum is the most pronounced.

Illustrations of various Applications of Charcoal in Experimental Investigations.

The gaseous products from minerals containing helium, hydrogen, &c., also the products from radium compounds,

cross section containing fused phosphorus, the whole being connected by means of a quill tube to a charcoal capsule, containing in part also a good layer of phosphoric anhydride, and the latter immersed in liquid air, the charcoal gradually absorbs the oxygen, and at a particular pressure the oxidation of the phosphorus vapour begins, and is revealed in the form of a phosphorescent glow, filling the whole of the glass bulb, which continues until the oxygen pressure gets too low. On removing the liquid air-bath, at a certain stage of the increasing pressure of oxygen, the bulb again becomes a glowing mass of phosphorescence, which wanes and disappears as the normal pressure is reached. This experiment may be repeated a great many times provided the phosphorus in the small side tube does not get into active combustion, which can always be avoided by a slight cooling. Such bulbs can be kept in the dark for months, and at the end of the time are quite active when cooled as described. A manometer attached to the side of the oxygen bulb shows that the oxygen pressure at the moment phosphorescence begins is only a fraction of a m.m. of mercury. From these results it appears that perfectly dry oxygen below 1 m.m. pressure combines with phosphorus.

The following experiment proving the absorption of carbonic acid, at a small partial pressure, by charcoal is very striking. A continuous stream of ordinary atmospheric air, containing three volumes of carbonic acid in ten thousand, is made to enter the apparatus, Fig. 4, at *A* and leave at *H*. It first passes through the jar, *B*, which contains some strong sulphuric acid, by which it is thoroughly dried. On leaving *B* the stream of air is divided at *C* into two portions, one of which passes through the jars *D*, *E*,

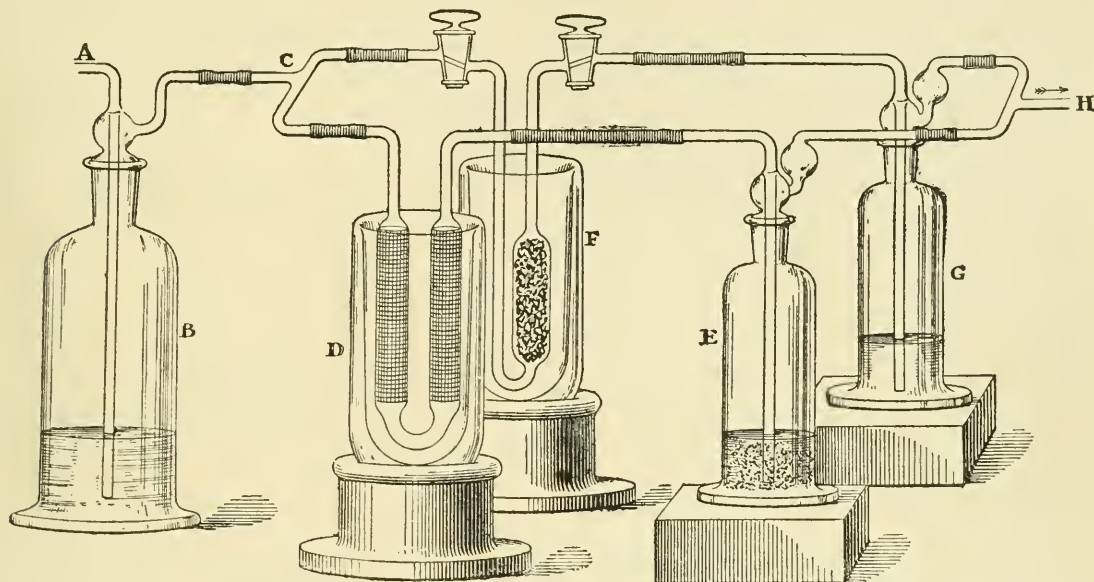


FIG. 4.

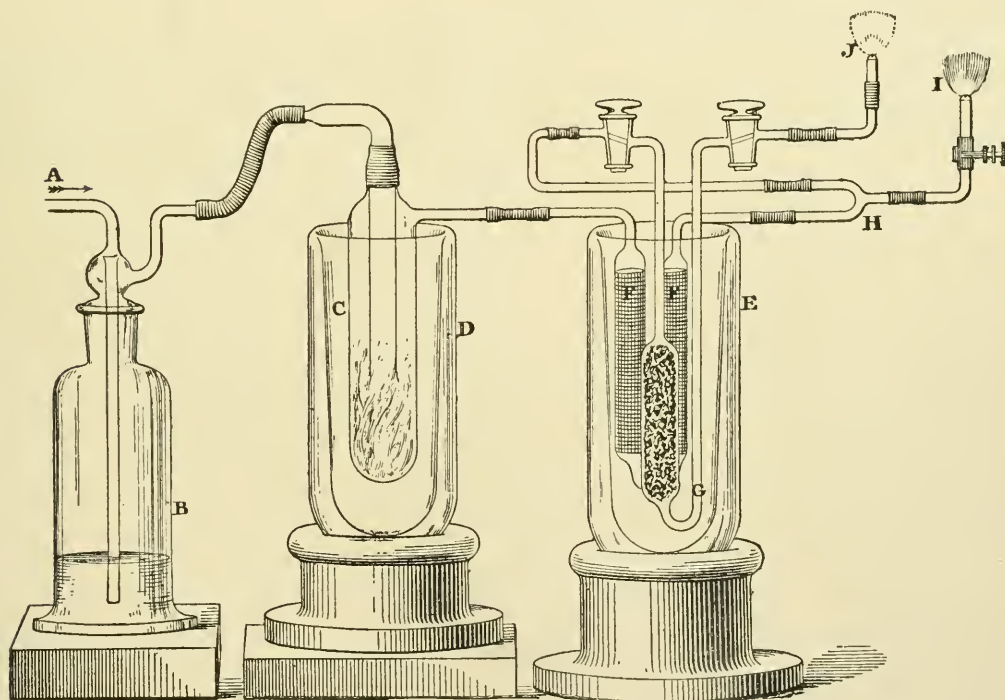


FIG. 5.

the other through the jars F, G, the two finally uniting and passing out at H. D and F are vacuum vessels containing solid carbonic acid, which maintains a temperature of -78°C . The air passes through a U-tube in D, the arms of which are filled with coils of copper gauze to ensure the complete reduction of its temperature to -78°C . It next

passes through the jar, E, containing some baryta water, which absorbs the carbonic acid remaining in it, before it emerges at H. The other stream of air passes in like manner through a U-tube in F, in one arm of which is a quantity of dry charcoal in small lumps; thence, after bubbling through some baryta water in the jar, G, it passes

to H, where it escapes. Now, the streams of air entering D and F are in exactly the same state, but while E shows by the milky deposit taking place that the one stream is still fully charged with carbonic acid after being thoroughly cooled to -78°C . in D, G shows by remaining permanently clear that a similar cooling of air to -78°C . in the presence of charcoal causes, for a time, complete absorption of the carbonic acid from the air, and this goes on until the charcoal absorbs about 1 per cent of its weight of carbonic acid.

The absorptive power of charcoal for hydrocarbons is shown in a similar manner by the following experiment:—Common coal-gas enters the apparatus in Fig. 5 by the tube at A, and after being dried by bubbling through strong sulphuric acid in the jar, B, has the less volatile gases condensed by passing through a vessel, C, cooled with carbonic acid snow, isolated in the vacuum vessel, D. The gas is further purified by percolating through the two copper coils contained in the arms of the U-tube, F F, immersed also in solid carbonic acid in the vacuum vessel, E, after which it passes on to H, where its path is bifurcated, one branch leading to I, where the issuing gas is lighted, while by the other branch the purified gas passes over charcoal in the U-tube, G, also at the temperature of solid carbonic acid, before proceeding to J, where it in turn is lighted. The difference between the two flames is very noticeable, that at I being quite luminous, while the other at J is non-luminous, like a Bunsen flame. The explanation is, that the charcoal at the temperature of -78°C . completely absorbs for a time all the hydrocarbons, such as marsh-gas and ethylene, upon which the luminosity of the flame of coal-gas depends, leaving practically carbonic oxide and hydrogen.

This preliminary investigation suggests many fields for further inquiry, and some of these I hope to deal with in future lectures.

My thanks are due to my chief assistant, Mr. Robert Lennox, F.C.S., for valuable aid in the conduct of the experiments; and Mr. J. W. Heath, F.C.S., has also helped in the progress of the work.

NOTE ON THE ESTIMATION OF HALOGENS IN ORGANIC SUBSTANCES.

By LESLIE HAMILTON BERRY, A.I.C.

THE process given below contains no new principle, but its merit lies in the rapidity and ease with which a result can be obtained, and hence commends itself to the notice of practical chemists. It is a combination of Piria and Schiff's heating the substance with lime in two crucibles, and Volhard's thiocyanate titration.

The substance is weighed into a very small platinum crucible, which is then filled up with a mixture of anhydrous sodium carbonate (1 part) and pure powdered quicklime (5 parts). The crucible is then inverted in a larger platinum crucible, the space between the two being filled up with the same mixture of sodium carbonate and lime.

The large crucible is now heated, first with a small blowpipe flame at the bottom of the crucible, and then more strongly heated till the mass is red-hot (duration of heating, one-half hour). The contents are then allowed to cool and dissolved in a large excess of dilute nitric acid (1 acid to 4 water). The substance is added slowly and the acid kept cold. Then add a known excess of N/10 AgNO_3 solution, stir vigorously, and heat on water-bath till clear; filter off the silver halide, wash thoroughly, and titrate the filtrate and washings with N/10 KCNS solution, using ammonium ferric alum as an indicator.

When the substance contains iodine, sodium carbonate must be used alone, so as to avoid formation of calcium iodate.

In order to obtain complete decomposition, it was found advisable to take a minimum quantity of the substance.

Results obtained by this Process.

Substance used: Chloral Hydrate, $\text{CCl}_3\text{CH}(\text{OH})_2$;
Calculated percentage Chlorine, 64.02.

	1.	2.
Weight of substance (gram.)	0.1120	0.2334
N/10 AgNO_3 required (c.c.)	20.25	42.20
≡ Weight chlorine	0.07188	0.14981
Chlorine (per cent)	64.18	64.22

Substance used: Dibrombenzene, $\text{C}_6\text{H}_4\text{Br}_2$;
Calculated percentage Bromine, 63.56.

	1.	2.
Weight of substance (gram.)	0.1480	0.2133
N/10 AgNO_3 required (c.c.)	11.75	16.95
≡ Weight chlorine	0.0940	0.1356
Chlorine (per cent)	63.51	63.55

In an estimation with iodoform, CHI_3 (calculated percentage iodine, 96.70), 0.3559 gram. required 27.14 c.c. N/10 AgNO_3 , which gives 96.84 per cent iodine.

The results obtained with dibrombenzene and iodoform are of considerable interest, because they show the applicability of this process to extremely volatile substances.

Technical College, Finsbury.

DETERMINATION OF MERCURY AND IODINE IN ANTISEPTIC SOAPS.

By ATHERTON SEIDELL.

THE germicidal character of the halogen salts of mercury has been recognised for a number of years, and comparative experiments, as quoted by Sternberg ("Text-book of Bacteriology," 1896, p. 188), have shown that the iodide has more than double the antiseptic value of the bichloride. It has been found by Thomson that mercuric iodide can be introduced into soap without forming an insoluble compound with the fatty acids or losing its antiseptic properties. (Thomson, *Journ. Soc. Chem. Ind.*, 1888, vii., 192. The *Journ. Soc. Chem. Ind.* reports the following patents obtained by Thomson:—"An Improved Antiseptic Soap," English Patent No. 9591, July 24, 1886; "Improvements in the Composition of Mercurial Soaps," No. 7117, May 16, 1887. The *Chemische Centralblatt* reports the German Patent, "Preparation of Antiseptic Soaps," D. R. P., No. 49,119, March 22, 1888). The mixture is effected by first dissolving the red iodide in a solution of an alkaline iodide and then incorporating it in the melted soap stock. Samples prepared in this manner were found by experiments upon a number of different organisms to be markedly germicidal in their action. More recent experiments along this line appear to have confirmed the observations of Thomson, and at present there are a number of mercuric iodide soaps on the market. Rideal, in his book upon "Disinfection and the Preservation of Food," 1903, Third Edition, p. 400, states that samples of mercuric iodide soap were found upon analysis to contain 0.37, 0.9, and 3.4 per cent, respectively, of potassium mercuric iodide. Neither the analytical procedure by which these determinations were made nor a reference to it are given by Rideal. Other reference books and a number of journals were examined without success for descriptions of such analyses.

Since no satisfactory method was found by which the mercury and iodine in these soaps could be quantitatively determined, the following investigation was undertaken.

The plan which first suggested itself was to decompose the fatty material by some suitable means and estimate the mercury and iodine in the residue obtained. Among the methods tried and found unsatisfactory for accomplishing this purpose were, first, treatment with fuming nitric acid both at the temperature of the steam-bath and in sealed tubes by the method of Carius; second, digestion in a

Kjeldahl flask with concentrated sulphuric acid; finally, alternate charring and extraction with acid.

The fatty acids could, of course, be removed from the acidified aqueous solution of the soap by filtration or shaking out with ether, but in either case an unavoidable error would result on account of the solubility of mercuric iodide in the fatty bodies, on the one hand ("Solubility of Mercuric Iodide in Fatty Bodies and in some other Solvents," Mèhu, *Journ. Pharm. Chim.*, 1885, [5], xii., 249), and its solubility in the immiscible solvents on the other ("Notice concerning the Solubility of Mercury Haloid Salts especially of Mercuric Iodide in Organic Solvents," Sulc, *Zeit. Anorg. Chem.*, 1900, xxv., 399; "On the Effect of various Solvents on the Allotropic Change of Mercuric Iodide," Kastle and Clarke, *Am. Chem. Journ.*, 1899, xxii., 473).

After considering all these points experiments were made as follows, using a sample of soap prepared in the laboratory by mixing a weighed amount of white toilet soap with a solution of mercuric iodide in potassium iodide:—Portions of this sample were dissolved in warm water, acidified with hydrochloric acid, and, after cooling, an immiscible solvent added to take up the separated fatty acids. Hydrogen sulphide was then passed through the two layers of solution until precipitation appeared complete. The two layers of solution were filtered together, and in some cases separately, but in spite of the greatest care a portion of the fatty material would separate from solution and remain on the sides of the Gooch crucible. Great difficulty was experienced in endeavouring to remove this deposit, and on this account it became necessary to modify the procedure.

After a number of trials it was finally ascertained that advantage could be taken of the solubility of the fatty acids in strong alcohol, to obtain a homogeneous solution of both the organic and inorganic constituents of the sample. The solution is best obtained by adding to the weighed sample of soap contained in an Erlenmeyer flask about 150 c.c. of 95 per cent alcohol, and 3 to 5 c.c. of concentrated hydrochloric acid. The solution is warmed, and successive small portions of water added until a perfectly clear solution is obtained on shaking. If suspended particles of impurities are present, the solution should, of course, be filtered. A slow stream of hydrogen sulphide gas is then passed through the liquid for about an hour, after which time the precipitated mercuric sulphide is filtered on a carefully prepared Gooch crucible. The fatty material present in the solution appears to have a tendency to cause the precipitate to pass through the filter, but no trouble on this account need be experienced, if care is taken to use the least amount of suction possible until the sulphide has been washed several times with 95 per cent alcohol. Although considerable time is required for this filtration, no great delay need be encountered, if a number of determinations are made simultaneously. The weight of mercuric sulphide obtained multiplied by 1.955 gives the amount of mercuric iodide in the weight of sample used.

The filtrate and washings from the mercuric sulphide are transferred to a beaker, and placed on the steam-bath. When the volume of the solution has been reduced to about one-half or one-third of the original volume, water is added to replace the alcohol, the solution cooled, and the separated fats removed by filtration. The clear solution obtained is placed in a glass stoppered separatory funnel together with 25 to 50 c.c. of chloroform. The combined iodine is then liberated by the addition of a few drops of nitrous acid. The iodine thus set free is quickly dissolved by the chloroform on shaking, and by repeating the operation two or three times the whole of the iodine is found in the chloroform solution. This latter is then washed by being shaken several times with distilled water. The washings are treated with fresh chloroform to recover any iodine which may have been taken up by them. Finally, the chloroform solution of the iodine is titrated to loss of colour with standard sodium thiosulphate solution. The number of c.c. required multiplied by the factor for

the standard solution gives the grms. of iodine in the sample used.

The nitrous acid solution is prepared by adding to a mixture of about 10 grms. of starch and 10 grms. of arsenious acid contained in a 700 c.c. Erlenmeyer flask about 150 c.c. of nitric acid of 1.3 specific gravity. The solution is warmed gently, and the reddish $\text{NO} + \text{NO}_2$ fumes conducted by means of a suitably bent glass tube into a bottle containing about 100 c.c. of concentrated sulphuric acid. The solution keeps well, and only a few drops are required at a time to liberate the iodine present in the solution under examination.

Results of the Determinations of the Mercury and Iodine in Soaps containing Mercuric Iodide.

Sample.	Soap taken.	Hgl ₂ added or claimed as present.	Hgl ₂ found.	I (total) found.	I as alkali iodide (calculated).
	Grms.	Per cent.	Per cent.	Per cent.	Per cent.
A ..	10.0	0.83	0.92	1.00	0.48
A ..	10.0	0.83	0.72	0.94	0.54
A ..	10.0	0.83	0.85	1.18	0.71
A ..	15.0	0.83	0.96	1.07	0.54
B ..	3.14	1.0	1.13	1.63	1.00
C ..	3.69	1.0	0.70	0.97	0.58
C ..	2.87	1.0	0.78	0.90	0.46
D ..	6.39	1.0	1.21	1.39	0.72
D ..	8.38	1.0	0.94	1.30	0.78
E ..	4.33	0.1	0.11	0.17	0.11
E ..	11.80	0.1	0.10	0.22	0.16
E ..	3.15	0.1	0.10	0.12	0.06

Sample A prepared in the laboratory.

B, C, and D, different samples of the same brand of soap.

Sample E, a purchased preparation.

The method as described above was used for the analysis of several samples of mercuric iodide soap prepared in the laboratory, and purchased samples of soap claimed to contain certain amounts of mercuric iodide. The results obtained are shown in the accompanying table.—*Journal of the American Chemical Society*, xxviii., No. 1.

A DELICATE COLOUR REACTION FOR COPPER,
AND A MICRO-CHEMICAL TEST FOR ZINC.

By HAROLD C. BRADLEY.

It has been known for a number of years that the extract of logwood-hæmatoxylin would produce with copper salts a dark blue colour of some intensity. One of the older and little used differential stains for tissues depended upon this reaction. The microtome section of tissue was immersed first in a copper solution, then washed and immersed again in a dilute solution of hæmatoxylin. Those portions of the tissue which fixed the copper would then be coloured dark blue, while the rest of the tissue remained uncoloured. In this way a stain is produced which will differentiate the cell nucleus from the surrounding cytoplasm. This same reaction was used by Herdman and Boyce ("Report of the Thompson-Bates Laboratories," Liverpool, ii., 1899) to demonstrate copper in the blood and tissues of the oyster, while Mendel and Bradley (*Am. Journ. Phys.*, 1905, xiv., 313) made use of it in localising the copper in the liver tissues of other marine molluscs. So far as we are aware, however, the reaction has never been used as a means of identifying small amounts of copper in solution, nor has it been realised of what extreme delicacy the reaction is susceptible.

Accordingly, a number of trials were made with copper sulphate solutions of varying strengths, to determine within what limits the reaction was available for the detection of copper, and also how the reaction compared in delicacy with other well-known tests for that element. Ferrocyanide,

ammonium sulphide, potassium iodide and starch are the reagents most commonly employed to detect small amounts of copper, and form some of the most delicate reactions of the laboratory. Potassium ferrocyanide gives, with dilute solutions of copper salts, a characteristic brown colour, becoming indistinguishable from the colour of the reagent when the copper solution contains less than 0.001 per cent of the metal. With starch paste and potassium iodide the reaction is slightly more delicate—cuprous iodide and starch iodide of characteristic deep blue being formed—but reaches its limit when the copper solution contains less than 0.001 per cent of the metal. On the other hand, the hæmatoxylin reaction is at its best in just such dilutions, and will serve to recognise copper in solutions of much greater attenuation. The following table shows, roughly, the comparative delicacy of these reactions:—

Per cent.	Reagent.		
	Ferrocyanide.	KI + starch.	Hæmatoxylin.
0.01	Brown	Blue	Blue
0.001 (Cu) ..	Brown	Blue	Blue
0.0001	?	Blue	Blue
0.00001	—	—	Blue
0.000001 ..	—	—	Blue
0.0000001 ..	—	—	Blue

That is, while under the most favourable conditions ferrocyanide of copper is formed visibly in solutions of one part copper in 100,000 parts of water, blue starch iodide in solutions of one part copper in 1,000,000 parts of water, the copper hæmatoxylin compound is distinctly recognisable in solutions of one part of copper in 1,000,000,000 parts of water. This is, we believe, one of the most delicate reactions known, chemical or physical, and is comparable with the physiological effects of copper salts on certain algæ, with the catalytic effect of copper in certain oxidations, and with the reactions for detecting radio-active bodies of extreme dilution. It is a thousand times more delicate than the ferrocyanide test for copper.

The possibilities for the use of such a reaction as a qualitative test for copper in drinking water from reservoirs treated with copper sulphate to destroy algæ, is at once apparent. Whether the reaction can be applied directly to the proximate analyses of drinking waters, what the conditions for optimum results are, and what the intensely blue copper compound is, are problems still to be worked out.

Zinc.—In carrying out some investigations on the normal presence and distribution of zinc in certain marine gastropods (Bradley, *Science*, 1903, xix., 196), the difficulty of recognising definitely small amounts of that metal in tissue ash containing relatively large amounts of copper, iron, calcium, and phosphoric acid, was found to be very great. Zinc forms practically no coloured compounds by which it may be identified in such a mixture, and the ordinary processes of separation are tedious and unsatisfactory. The desirability of finding some rapid and reliable test for zinc led to a thorough canvassing of the less common laboratory reagents for precipitating that metal, and the finding of a microchemical test which proved to be adequate in every way. The reaction is by no means a new one, but its possibilities as a reliable test for zinc seem to have been overlooked.

A moderately concentrated solution of a zinc salt when treated with sodium nitro-prusside throws down a salmon-pink precipitate of zinc nitro-prusside, fairly insoluble in cold water, much less so in hot. The characteristic feature of this precipitate is its definite and readily identified crystal form. All the other insoluble nitro-prussides of the heavy metals are amorphous, slimy precipitates resembling the ferrocyanides in general physical properties. Thus, even in a mixture of several metallic salts, such as copper, silver, cobalt, zinc, &c., the zinc nitro-prusside can be recognised under the microscope by the presence of its characteristic crystals in the amorphous mass of the other nitro-prussides. In performing the test,

it is desirable to have the solution of the salts fairly concentrated—about 10 per cent strength is convenient—and to remove the copper by H_2S . In such solutions of tissue ash as were used in our experiments, copper was first removed, and the filtrate containing iron, calcium, phosphoric acid, &c., concentrated to small bulk. A drop of this solution placed on a microscope slide and digested with a drop of the freshly prepared nitro-prusside solution, deposited on cooling the rectangular plates and prisms of the zinc salt when that metal was present in such minute amounts that the ordinary methods of separation and identification failed to show it definitely, or required the ashing of large amounts of the original material. For example, by this method zinc was detected readily in the blood of certain molluscs in a few minutes, while by the ordinary methods of separation and analysis—the basic acetate method, or better, the precipitation of the metal as sulphide from a formic acid solution—many hours are required to ash sufficient material and carry through the steps of the analysis.—*American Journal of Science*, xxii., No. 130.

THE COMBUSTION OF HALOGEN COMPOUNDS IN PRESENCE OF COPPER OXIDE.

By CHARLES J. ROBINSON.

IN the course of some work by J. Bishop Tingle and the author of this note, occasion arose for determining carbon and hydrogen in certain compounds containing a halogen, and an attempt was made to do away with the necessity for preparing a combustion tube filled with lead chromate by suitably modifying the ordinary tube containing copper oxide. This purpose was accomplished simply and satisfactorily in the following manner:—

A cartridge, similar to that employed by Morse and Taylor in the analysis of sulphur compounds (*Am. Chem. Journ.*, xxxiii., 602), was made by rolling a small piece of heavy copper wire gauze into the form of a hollow cylinder, which was only 6 or 7 c.m. long, and just fitted into the combustion tube. The cylinder was filled with pure lead chromate, the ends closed by wrapping with copper wire, which also passed lengthwise through the cartridge, and was looped at each end to facilitate removal from the tube. The copper parts were oxidised by ignition. When it was desired to analyse halogen compounds, this cartridge was placed just in front of the boat, in a combustion tube filled in the ordinary way with copper oxide. In burning, care was taken that the part of the tube containing the cartridge was well heated before decomposition of the substance began, but no other special precautions were found necessary. If the space in the tube, or the decomposition temperature of the substance to be analysed demand it, the oxidised spiral in front of the boat should, of course, be removed and the cartridge be allowed to occupy its place.

The advantages gained by the use of this device are that combustions of halogen compounds can be made just as readily as combustions of ordinary compounds, and that the same tube can be used for both. The cartridge may be removed or not, as the operator pleases, to make ordinary analyses subsequent to analyses of substances containing halogens. The same cartridge may be used repeatedly, but no statement can be made as to the number of times it can be employed safely without renewal, because of the great variation in content of halogen in different compounds. The life of the tube itself is not affected as it is when the tube is entirely filled with lead chromate.

The method has been found to be so completely satisfactory that it is judged decidedly preferable, in very many cases, to determine carbon and hydrogen rather than halogen for the identification of new compounds. The time required for the analysis is much shorter, and the figures for the content of carbon and hydrogen in complex

bodies are usually much more distinctive than those for the content of halogen.

No special experiments have been conducted to test the method, but the analyses given below were made in the course of the investigation referred to. The substances analysed are products of the action of β -bromophenylhydrazine on camphoroxalic acid. Only the one determination of carbon and hydrogen was made in each case.

I. A compound, $C_{18}H_{23}O_4N_2Br$, melting at 149° with decomposition.

0.2409 grm. substance gave 0.4603 grm. CO_2 and 0.1150 grm. H_2O .

	Calculated.	Found.
C	52.53	52.14
H	5.63	5.34

II. A compound, $C_{18}H_{21}O_3N_2Br$, melting at 172° with decomposition.

0.2135 grm. substance gave 0.4308 grm. CO_2 and 0.0982 grm. H_2O .

	Calculated.	Found.
C	54.94	55.03
H	5.38	5.15

III. A compound, $C_{20}H_{23}O_2N_2Br$, m. p. 107° .

0.2125 grm. substance gave 0.4624 grm. CO_2 and 0.1045 grm. H_2O .

	Calculated.	Found.
C	59.52	59.35
H	5.75	5.50

IV. A compound, $C_{18}H_{19}O_2N_2Br$, melting at 215° with decomposition.

0.1937 grm. substance gave 0.4095 grm. CO_2 and 0.0923 grm. H_2O .

	Calculated.	Found.
C	57.58	57.66
H	5.10	5.33

The method has also been applied to the determination of nitrogen in halogen compounds. The cartridge of lead chromate is placed just in front of the substance to be burned, and the latter is mixed with lead chromate. Otherwise the tube is filled in the ordinary way with copper oxide. The results obtained are shown in the following analysis:—

I. The compound $C_{18}H_{21}O_3N_2Br$.

0.2624 grm. substance gave 16.2 c.c. N_2 at 19° and 758 m.m.

	Calculated.	Found.
N	7.14	7.08

The determination of carbon and hydrogen in sulphur compounds could, doubtless, be accomplished in the same manner, in the presence of copper oxide, but no experiments have been made in this direction.—*American Chemical Journal*, xxxv., No. 6.

ON THE COMPOSITION OF PETROLEUM.*

THE SULPHUR COMPOUNDS AND UNSATURATED HYDROCARBONS IN CANADIAN PETROLEUM.

By CHARLES F. MABERY and WILLIAM O. QUAYLE.

(Continued from p. 183).

Octodecyl Thiophane.

(Fraction 290—295°, $C_{18}H_{36}S$).

FROM 350 grms. of the vacuum distillate $191-210^\circ$ (50 m.m.), alcoholic mercuric chloride gave a very thick viscous precipitate, from which was obtained, after the second precipitation, 50 grms. of a dark coloured oil that collected, after continued distillation *in vacuo*, nearly colourless, for

the most part at $198-202^\circ$. Under atmospheric pressure this oil distilled, with some decomposition, at $290-295^\circ$; sp. gr. at 20° , 0.9235. The values obtained by analysis corresponded to the formula $C_{18}H_{36}S$.

I. 0.2005 grm. oil gave 0.5602 grm. CO_2 and 0.2214 grm. H_2O .

II. 0.1937 grm. oil gave 0.1634 grm. $BaSO_4$.

III. 0.2011 grm. oil gave 0.1636 grm. $BaSO_4$.

	Calculated for $C_{18}H_{36}S$.	Found.		
		I.	II.	III.
C	76.06	76.22	—	—
H	12.67	12.35	—	—
S	11.27	—	11.57	11.18

We have made no attempts toward the separation of sulphur compounds with higher molecular weights, but there is no doubt that higher homologues are contained in the less volatile distillates which we have separated from the original oil. It is probable that intermediary members of this series are contained in the distillates examined, and that they might be identified in larger quantities of material.

As has been shown in the method of preparation, the thiophanes combine readily with alcoholic mercuric chloride to form viscous oils. They also form addition products with chlorplatinic acid, which are heavy viscous oils. When heated in a sealed tube with ethyl iodide, addition products are formed, which crystallise in small prisms— $C_nH_{2n}S$, C_2H_5I . These addition products form alkaline hydroxides when warmed with silver oxide and water:—



Bromine exerts a characteristic action on these sulphur compounds. Immediately when they come in contact combination follows with almost explosive violence and copious evolution of hydrobromic acid, in equivalent amounts to the bromine added. It is wholly unlike the behaviour of unsaturated hydrocarbons with bromine. Probably part of the bromine combines with the sulphur, but the evolution of hydrobromic acid begins immediately, doubtless due to the ready replacement of the methylene hydrogen atoms.

The thiophanes still further resemble the well-known series of sulphur derivatives in their behaviour toward oxidation. The formation and properties of the sulphones will be described later.

In addition to the analytical data that establish the composition of the thiophanes, we have determined their indices of refraction, and the corresponding molecular refraction verifies the formulæ given by analysis.

Indices of Refraction of the Thiophanes.

Many attempts were made, with different solvents, to determine the molecular weights of the sulphur compounds in Canadian petroleum, but no concordant values could be obtained, even with the same substance and the same solvent.

Better success, however, was reached in ascertaining the indices of refraction, but since the values for sulphur in organic compounds have not been determined with the same certainty as in the case of carbon, hydrogen, and oxygen, some attention was given to verifying this constant.

The index of refraction found by Nasini for ethyl sulphide was 1.44233; for ethyl mercaptan, 1.43055; and for ethyl disulphide, 1.50633.

Assigning the accepted values to carbon and hydrogen, the calculated value for sulphur becomes—for ethyl sulphide, 7.98; for ethyl mercaptan, 7.81; and for ethyl disulphide, 8.03. In determining the value of sulphur in ethyl mercaptan, we found the angle to be $49^\circ 24'$, which corresponds to the index 1.4323, and the calculated value for sulphur is 7.89.

Isobutyl sulphide gave us 1.4585 as its index of refraction,

* Contributions from the Chemical Laboratory of Case School of Applied Science. From the *American Chemical Journal*, xxxv., No. 5

calculated from the observed angle $44^{\circ} 57'$; the corresponding molecular refraction is 46.85. Assigning the accepted values to carbon and hydrogen, the difference is the value of sulphur, 7.98, the same as the value calculated from Nasini's index of ethyl sulphide.

The index assigned to thiophen is 1.5268, which gives as its molecular refraction 24.12, leaving a value for sulphur 6.53. Thiophen is assumed to have two sets of double bonds. The petroleum sulphur compounds under consideration, although doubtless possessing a ring structure, apparently do not contain carbon atoms connected by double linkage. We have therefore considered it safe to use the value 7.98 for sulphur, and the following molecular refraction for the petroleum sulphur compounds were calculated on the basis of this value:—

Heptyl Thiophane.

The fraction 74—76° (50 m.m.), which proved to contain heptyl thiophane, gave as its index of refraction 1.468, corresponding to the following molecular refraction:—

Calculated for $C_7H_{14}S$	40.15
Found	40.82

Octyl Thiophane.

From the fraction 83—85° (50 m.m.) was separated octyl thiophane. Its index of refraction was found to be 1.4860, and its molecular refraction—

Calculated for $C_8H_{16}S$	44.75
Found	44.91

Nonyl Thiophane.

Nonyl thiophane was found to be the principal constituent of the fraction 106—108° (50 m.m.). It gave as its index of refraction 1.4746, from which was calculated its molecular refraction:—

Calculated for $C_9H_{18}S$	49.35
Found	49.50

Decyl Thiophane, $C_{10}H_{20}S$.

The index of refraction of the distillate 114—116°, from which was separated decyl thiophane, we found to be 1.4766. Its molecular refraction was calculated as follows:—

Calculated for $C_{10}H_{20}S$	53.94
Found	53.60

Undecyl Thiophane.

Undecyl thiophane was found in the fraction 130—135° (50 m.m.). We found its index of refraction to be 1.480, and its molecular refraction—

Calculated for $C_{11}H_{22}S$	58.54
Found	58.53

Quatdecyl Thiophane, $C_{14}H_{28}S$.

The fraction 168—170° gave quatdecyl thiophane. Its index of refraction, 1.4892, corresponded to the molecular refraction:—

Calculated for $C_{14}H_{28}S$	72.33
Found	71.61

Sextdecyl Thiophane.

This sulphur compound was found in the fraction 184—186° (50 m.m.). Its index of refraction proved to be 1.4903, from which its molecular refraction was calculated:—

Calculated for $C_{16}H_{32}S$	81.52
Found	80.44

The index of refraction of octadecyl thiophane was found to be 1.4977, but the molecular refraction calculated from this value and its sp. gr. (0.9625 at 20°) gave a value different by four units from the calculated molecular refraction.

Oxidation Products of the Thiophanes.

Appreciating the importance of oxidation products in ascertaining the composition of the thiophanes, we have tried very thoroughly the action of oxidation agents—nitric acid, chromic acid, and potassium permanganate. These sulphur compounds absorb oxygen with great readiness, and the reaction must be carefully controlled to prevent ultimate oxidation to sulphuric acid. It was not found possible to limit the oxidation to the formation of the sulphoxide, since the sulphone seems to be the more stable condition. Nitric acid readily oxidises the sulphur with an extremely violent reaction, but apparently also forms nitro-derivatives, since the products contain nitrogen.

Chromic acid oxidises the sulphur readily, with some danger that the reaction proceeds to ultimate oxidation. Potassium permanganate, in either alkaline or acid solution, readily effects the change, with little danger of the formation of sulphuric acid. After careful study of the conditions, it was found that the largest yield of oxidation product was obtained by adding slowly to the oil 1.5 times the calculated weight of permanganate dissolved in thirty times its weight of water, keeping the solution cold. With efficient cooling, the permanganate can be added as rapidly as it is decolorised. After the reaction was complete, the precipitated manganic oxide was filtered and the solution distilled with steam, which carried over any unoxidised sulphur compound, leaving behind the oxidation product. When carefully conducted, the solution shows no sulphuric acid. From the residue of the steam distillation the oxidation product was extracted with ether, and the ether evaporated, leaving a thick heavy oil, which increased in viscosity with increase in molecular weight. In several instances we dissolved the precipitated manganic oxide by saturating with sulphurous oxide and extracted with ether. When the oxidation is complete this is the easier method; but distillation with steam ensures the removal of any decomposition products.

The action of oxidising agents showed a wide difference in deportment between the sulphur compounds from Canadian petroleum and sulphides synthetically prepared. For example, synthetic isoamylsulphide, allowed to stand with concentrated nitric acid, showed vigorous reaction only after several minutes, with evolution of heat. After the reaction ceased, heat was applied and water added. The oxidation product collected above the water and partly dissolved. Only a trace of sulphuric acid was found in the solution. On treating the sulphur compounds from Canadian petroleum in the same manner, the reaction was much more vigorous, with immediate evolution of heat. The product formed a thick oil, heavier than water, and much sulphuric acid was formed, but the oxidised oil contained much sulphur, showing that it consisted in part of an oxidised sulphur compound. This difference in the action of nitric acid is pretty conclusive proof that the sulphur compounds under consideration are not alkyl sulphides, nor, indeed, members of any other well-known series. It is in accordance with the observation that the hydro-ring compounds, the methylenes, are less stable towards reagents than the aromatic or paraffin compounds.

Hexyl Thiophane Sulphone.

The presence of hexyl thiophane was indicated in the fraction 125—130° (atmospheric pressure), although it was not separated in a pure form. In attempting to prepare the sulphone, the fraction 55—57° (50 m.m.) was treated, as described above, with potassium permanganate. Oxidation was rapid, even when cooled to 0°. In this instance, after dissolving the manganic oxide in sulphurous acid, the solution was evaporated to dryness and the residue extracted with anhydrous ether. Evaporation of the ether left a thick viscous oil with a sweetish taste and odour, with no reaction for sulphuric acid. While the analytical values obtained indicated that the hexyl compound was contaminated with a higher homologue, it is evident that hexyl thiophane was the principal constituent.

Analysis.—C, 49.39; H, 8.47; S, 19.02. Required for $C_6H_{12}SO_2$ —C, 48.64; H, 8.11; S, 21.62.

Heptyl Thiophane Sulphone, $C_7H_{14}SO_2$.

The oxidation of heptyl thiophane was conducted as described above. After neutralising with sodium carbonate and evaporating to dryness, the residue was extracted with anhydrous ether. No sulphuric acid was formed by the oxidation. *Analysis* :—

- I. 0.1992 grm. substance gave 0.3801 grm. CO_2 and 0.1531 grm. H_2O .
II. 0.1628 grm. substance gave 0.2279 grm. $BaSO_4$.

	Calculated for $C_7H_{14}SO_2$.	Found.	
		I.	II.
C	51.86	52.05	—
H	8.64	8.59	—
S	19.75	—	19.23

This sulphone formed a very thick heavy oil. Its sp. gr. was found to be 1.1138 at 20°.

Octyl Thiophane Sulphone, $C_8H_{16}SO_2$.

Fifty grms. of the fraction 87—89°, identified as octyl thiophane, was oxidised carefully at 0°. After dissolving the manganic oxide and distilling with steam, 36 grms. of a heavy oil separated, with no formation of sulphuric acid. After neutralising with sodium carbonate, evaporating to dryness, and extracting with ether, this oil gave as its sp. gr. at 20° 1.1142. *Analysis* :—

- I. 0.1697 grm. substance gave 0.3385 grm. CO_2 and 0.1368 grm. H_2O .
II. 0.2038 grm. substance gave 0.2702 grm. $BaSO_4$.

	Calculated for $C_8H_{16}SO_2$.	Found.	
		I.	II.
C	54.55	54.41	—
H	9.11	9.01	—
S	18.18	—	18.21

Nonyl Thiophane Sulphone, $C_9H_{18}SO_2$.

For oxidation of the nonyl sulphur compound, the fraction 106—108° (50 m.m.) was selected. In the first half of the oxidation the potassium permanganate was added slowly in a bath of ice and salt. The reaction was completed at ordinary temperatures, and it proceeded much more slowly toward the end. The required amount of permanganate was consumed in four days, and no sulphuric acid was formed. In all these oxidations, doubtless, sulphonic acids were formed to some extent, but their removal was ensured by neutralising with sodium hydroxide and extraction of the evaporated residue with anhydrous ether. The sp. gr. of the nonyl sulphone was found to be 1.1161 at 20°. *Analysis* :—

- I. 0.1867 grm. substance gave 0.3874 grm. CO_2 and 0.1509 grm. H_2O .
II. 0.1679 grm. substance gave 0.2071 grm. $BaSO_4$.

	Calculated for $C_9H_{18}SO_2$.	Found.	
		I.	II.
C	56.83	56.61	—
H	9.47	9.04	—
S	16.84	—	16.93

Undecyl Thiophane Sulphone, $C_{11}H_{22}SO_2$.

We were unable to isolate an oxidation product which corresponded closely in composition to decyl thiophane sulphone from the original fraction, and the amount of the thiophane isolated was not sufficient for oxidation.

Undecyl thiophane sulphone was prepared from the undecyl thiophane separated from the fraction 129—131°

(50 m.m.); 7.8 grms. of the thiophane gave 5 grms. of the oxidation product. The heavy oil left after distillation with steam had a pleasant sweetish odour; its sp. gr. was found to be 1.1126 at 20°. *Analysis* :—

- I. 0.1903 grm. substance gave 0.4176 grm. CO_2 and 0.1621 grm. H_2O .
II. 0.1470 grm. substance gave 0.1579 grm. $BaSO_4$.

	Calculated for $C_{11}H_{22}SO_2$.	Found.	
		I.	II.
C	60.54	59.84	—
H	10.09	9.53	—
S	14.68	—	14.75

Dodecyl Thiophane Sulphone, $C_{12}H_{24}SO_2$.

After treating 7 grms. of the distillate 142—144° (50 m.m.) with 9 grms. of potassium permanganate, the proportions found most suitable, there still remained a slight odour of the thiophane, which was completely removed by distillation with steam. The oil that remained after extraction of the steam residue with ether gave as its sp. gr. at 20° 1.1372. *Analysis* :—

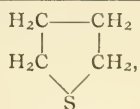
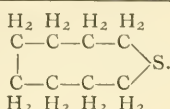
- I. 0.1533 grm. substance gave 0.3483 grm. CO_2 and 0.1402 grm. H_2O .
II. 0.1645 grm. substance gave 0.1554 grm. $BaSO_4$.

	Calculated for $C_{12}H_{24}SO_2$.	Found.	
		I.	II.
C	62.07	61.98	—
H	10.35	10.23	—
S	13.79	—	12.91

The sulphur compounds in Canadian petroleum have been shown to belong to a series C_nH_{2n} . Their structure must be explained either as unsaturated, like the ethylene sulphides, or by a ring arrangement. That these bodies are not of the ethylene series is shown by the facts that the ethylene sulphides are solids, and that they absorb bromine without evolution of hydrobromic acid. The petroleum sulphur compounds have a very high specific gravity, and they evolve hydrobromic acid copiously when treated with bromine. They resemble the well known series of sulphur compounds in forming addition products with mercuric chloride, in the formation of sulphones, the formation of addition products with alkyl iodides, and alkaline hydroxides.

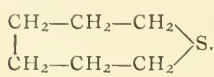
In a former paper by Mabery and Smith it was shown that the sulphur compounds in petroleum are not mercaptans nor thiophenes. The series separated by Mabery and Smith from Ohio petroleum formed crystalline addition products with alcoholic mercuric chloride, and the sulphur oils themselves resemble the alkyl sulphides. But the series contained in the portions of Canadian petroleum with higher boiling-points are not alkyl sulphides, mercaptans, thiophenes, nor ethylene sulphides. Their high specific gravity shows that they belong to a new series. The cyclic condition of the constituents of Pennsylvania, Ohio, Canadian, Texas, and California petroleum corresponding to the series C_nH_{2n} , C_nH_{2n-2} , C_nH_{2n-4} , &c., has been described in former papers, and the proportions of these series are indicated by the differences in specific gravity. Canadian petroleum is composed for the most part of the series of hydrocarbons poorer in hydrogen. Other constituents of petroleum partake of a similar cyclic condition. The nitrogen compounds, for example, in California petroleum, are tetrahydro and octahydro bodies, with a structure resembling that of the hydroquinolines.

Empirically, the thiophanes are hydrothiophenes with long side chains, methylene sulphides with numerous or long side chains, or simple ring methylene sulphides. Either class of formulæ will satisfy the results of analysis. For example :—

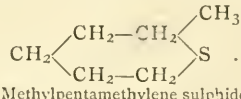
Tetrahydrothiophene
or pentamethylene sulphide.

The ready formation of sulphones, addition products with alkyl iodides and hydrates is unlike the thiophens, but the hydrothiophens may behave differently. It is improbable that rings with a very large number of carbon atoms can exist. A condensed ring structure like quinoline or naphthoquinoline with sulphur in place of nitrogen, is excluded by the series C_nH_{2n} .

As shown above, the lowest member of the series separated from Canadian petroleum was $\text{C}_6\text{H}_{12}\text{S}$, boiling-point $45-50^\circ$ (50 m.m.), which may be hexamethylene sulphide, or methylpentamethylenesulphide. Higher homologues may reasonably be considered as side chain derivatives:—



Hexamethylene sulphide.



Methylpentamethylene sulphide.

The structure of these bodies will doubtless have to be referred to the methylene ring, yet the precise form of the ring with reference to the number of carbon atoms it contains is still uncertain. For instance, the central group may be a penta-, hexa-, or hepta-methylene ring. It has therefore seemed advisable to employ a comprehensive name that shall include any possible arrangement, and the term thiophane has been adopted. Without doubt, the structure of these sulphur derivatives will be defined with greater precision when the structure of the hydrocarbons of the series C_nH_{2n} , $\text{C}_n\text{H}_{2n-2}$, $\text{C}_n\text{H}_{2n-4}$, &c., which constitute the greater part of the constituents of petroleum with high boiling-points from any source, are better understood.

To be continued).

NOTICES OF BOOKS.

Thirtieth Annual Report of His Majesty's Inspectors of Explosives. London: Darling and Son, Ltd. 1906.

The Annual Report for 1905 of His Majesty's Inspectors of Explosives calls attention to the modifications of the law during the year, and describes the results of inspections, giving statistics of the manufacture and storage of explosives, and details regarding their packing, conveyance, &c. It contains the report of the Department's Chemical Adviser, Dr. Dupré, F.R.S., in which is described the research work which is still being continued, and which has apparently not brought to light during the year any facts of great importance. Much space is given to the discussion of accidents caused by explosives and the means adopted to prevent them, while the experiments witnessed by the Inspectors are shortly alluded to, though Dr. Dupré's important investigations with lance composition in connection with an accident at Messrs. Jennison and Co.'s factory are not included, being contained in a special report.

The Chemical Analysis of Iron. By ANDREW ALEXANDER BLAIR. Sixth Edition. Philadelphia and London: J. B. Lippincott Company. 1906.

ALTHOUGH this book has perhaps been used more widely in America than in this country, and gives greater prominence to methods generally adopted in the United States, English chemists will no doubt welcome a new edition. All really useful methods are included, and new chapters have been

added on chrome-tungsten steels and on ferro-tungsten and tungsten metal, while the importance of the methods of separation and determination of the alloys of the rarer metals, tungsten, chromium, nickel, vanadium, molybdenum, &c., is full recognised, and special attention is paid to them. Many useful suggestions for apparatus will be found worthy of the notice of others besides iron chemists, and the excellent diagrammatic illustrations greatly simplify the instructions for experimental work. New and improved methods of determining carbon in iron and steel are given, and the analysis of iron ores, limestone, slags, &c., is discussed, while simple methods of gas analysis are also included.

The Chemistry of Paints and Paint Vehicles. By CLARE H. HALL, B.S. London: Archibald Constable and Co., Ltd. 1906.

THERE is undoubtedly room for a short and concise work dealing exclusively with the chemistry of paints, and as such this book will probably be cordially welcomed. In it is given an outline of methods of determining and separating the elementary constituents of paints, for the fuller treatment of which the student would perhaps find it necessary to refer to larger books. Methods of applying strength tests to raw materials are next considered, as well as their properties and estimation, and the analysis of dry colours, pastes, and liquid paints is fully described, both qualitative and quantitative processes being included. The succeeding chapter, on the matching of samples, will be found specially useful and interesting by chemists employed in works for the manufacturing of paints; it contains clear directions for the procedure to be adopted in various cases, while the analysis of oils is also treated very shortly, the author showing considerable judgment in the suggestions for the tests best used by those who are not skilled in oil analysis. The physical characteristics of varnishes and thinners are then briefly described, the quantitative determination of adulterations in turpentine being included.

Handbuch der Sprengarbeit. ("Handbook of Blasting"). By OSCAR GUTTMANN. Second Edition. Braunschweig: Friedrich Vieweg und Sohn. 1906.

THE second edition of this well-known text-book, like the first, devotes more attention to practice than theory, and the author has endeavoured to make it specially complete as regards boring machines and blasting materials, which it treats at considerable length. Many new illustrations are included, and the most recent publications have been carefully abstracted, while modern theories are shortly discussed, and a summary is given of those which are to be regarded as important. Blasting operations are described in detail, and the text is arranged systematically, so that the book is an excellent specimen of a convenient work of reference, upon the production of which the author may be congratulated, for the work of collecting and abstracting such a widely scattered literature is a task which calls for no small amount of patience and skill.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

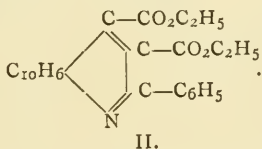
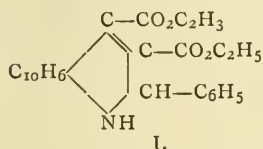
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 12, September 17, 1906.

Action of Fluorine on Chlorine. A New Method of preparing Hypochlorous Acid.—Paul Debeau.—As a result of a long series of researches, M. Moissan came to the conclusion that, at either ordinary or high temperatures,

fluorine and chlorine have no reaction on one another, either directly or indirectly. The author now investigates the action of fluorine on chlorine at low temperatures, making two series of experiments—one series when working in presence of excess of fluorine, the other in presence of excess of chlorine. He finds that fluorine and chlorine never unite directly. Liquid chlorine dissolves fluorine, but the fluorine is given off again at the solidification-point of chlorine. In presence of water, however, fluorine oxidises chlorine, transforming it completely into hypochlorous acid. This constitutes a new method of preparation of hypochlorous acid: $\text{H}_2\text{O} + \text{Cl} + \text{F} = \text{HF} + \text{ClOH}$.

Syntheses in the Quinoleic Group. Phenyl-naphtho-quinoleindicarbonic Acid and its Derivatives.—L. J. Simon and Ch. Minguin.—The product which predominates during the action of oxalacetic ether on benzylidene- β -naphthylamine is an addition compound, $\text{CO}_2\text{C}_2\text{H}_5\text{—CO—CH—CO}_2\text{C}_2\text{H}_5$.

When subjected to the condensing action of strong sulphuric acid in the cold, this is transformed into the cyclic compound (I.), after which oxidation by chromic acid regularly transforms it into dicarboxylic phenyl-naphthoquinoleinic ether (II.).



These results were predicted by L. J. Simon and A. Conduché. After a long investigation the authors now confirm them, and they also find the conditions of saponification of dicarboxylic phenyl-naphthoquinoleinic ether, and the properties of the resulting acid bodies.

Action of Mixed Organo-magnesium Compounds on the Imides.—Constantine Béis.—The author uses mixed compounds of methyl iodide, methyl bromide, ethyl bromide, and phenyl bromide of magnesium, and he finds that only when these compounds are used in a nascent state are satisfactory results obtained, except in the case of methyl iodide, the latter giving a simple molecular addition product. However, in the nascent state he obtains a series of compounds to which the formulæ of isoindolinones are attributed, these being isomers of the phenylamidoketones. The author selects the former because they agree with the results of the preliminary experiments which he makes on the constitution of the bodies. He is continuing his investigations on this subject.

No. 13, September 24.

This number contains no chemical matter.

MISCELLANEOUS.

Appointment.—Dr. H. A. D. Jowett has been appointed manager of the works of Burroughs, Wellcome, and Co., in place of Mr. A. T. Hill, who has resigned.

New Qualitative Test for Calcium.—F. F. Flanders.—The difficulty of testing for calcium in the presence of barium and strontium led the writer to turn his attention to a test for this metal which would not be answered by barium and strontium. In this connection the action of potassium ferrocyanide has been tried with surprisingly good results, so good in fact that it seems almost impossible that the reaction has not been used before in this connection. As only one reference could be found to the action

of potassium ferrocyanide on calcium compounds (Prescott and Johnson, 1903, p. 212), the fear of repetition is braved and the test described, in the hope that it may prove useful. In separating barium, strontium, and calcium, the commonly accepted method seems to be precipitation with ammonium carbonate in ammoniacal solution, solution of the washed precipitate in acetic acid, removal of barium by potassium chromate or bichromate, re-precipitation of strontium and calcium by ammonium carbonate in ammoniacal solution, re-solution of the precipitate in acetic or hydrochloric acid, removal of strontium by ammonium sulphate, and finally testing for calcium by addition of ammonium oxalate in ammoniacal solution. The weak point in this scheme is the danger of traces of barium and strontium remaining in solution, with the well-known effect on the calcium test. The suggested procedure is the same as the foregoing up to the point of the re-solution of the precipitate after barium has been removed (except that acetic acid only should be used). At this point the solution is divided, and calcium sulphate added to one portion to test for strontium. To the other portion an equal volume of ammonium chloride is added, and a few c.c. of potassium ferrocyanide. The presence of calcium is indicated by the formation of a light yellowish green precipitate. The sensitiveness of the test has been tried on standard solutions of calcium salts, and when applied directly to the calcium solutions was found to indicate 1 part of calcium in 7000 parts. The ammonium oxalate test was also tried, and was found to indicate 1 part in 140,000 parts. The oxalate test was also applied to a series of standard calcium solutions to which strontium had been added. The strontium was removed by ammonium sulphate as in the first method outlined. Under these conditions the addition of ammonium oxalate caused no precipitate in solutions more dilute than 1 part in 14,000. The difference is accounted for by the fact that the ammonium sulphate precipitates out a large amount of calcium with the strontium, and by the fact that calcium oxalate is probably more soluble in ammonium sulphate than in water. The ferrocyanide test was also tried in the regular scheme of analysis, and clearly indicated 1 part in 7000. This 1 part in 7000 seems to be the solubility limit of the calcium-potassium ferrocyanide. Under similar conditions and within the limits of the ferrocyanide test, the volume of the precipitate is about four times as great with ferrocyanide as with oxalate. It might be added that comparatively fresh solutions of potassium ferrocyanide seem to give the best results.—*Journal of the American Chemical Society*, xxviii., No. 10.

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1883 TO 1902.NOTICE IS HEREBY GIVEN that
GEORGE WILLIAM JOHNSON, of 47, Lincoln's Inn Fields, in
the County of London. Patent Agent, seeks leave to amend the
Specification of Letters Patent No. 22,736 of 1905, granted to him for
"Improvements in the Manufacture of Organic Compounds con-
taining Sulphur, and of Red Colouring Matter therefrom."Particulars of the proposed amendment were set forth in the Illus-
trated Official Journal (Patents), issued on the 10th October, 1906.Any person, or persons, may give Notice of Opposition to the
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THE CHEMICAL NEWS.

VOL. XCIV., No. 2448.

SOME APPLICATIONS OF THE THEORY OF ELECTRIC DISCHARGE TO SPECTROSCOPY.*

By Prof. JOSEPH JOHN THOMSON, M.A., D.Sc., F.R.S., &c.,
Professor of Natural Philosophy, R.I.

THE luminosity produced by an electric current passing through a gas at low pressure varies greatly in character, not only when we alter the nature of the discharge—as, for example, when we pass from the arc to the spark—but also in many cases at different points of the same discharge. The luminosity may be of one colour at one place and of a very different one at another; a spectroscopic examination shows the spectrum of the same gas often varies considerably as we proceed along the line of discharge. As recent experiments have thrown a considerable amount of light on the processes going on in the different kinds of electrical discharge and at different parts of the same discharge, the study of the connection between the changes in the electrical effects and the changes in the spectra

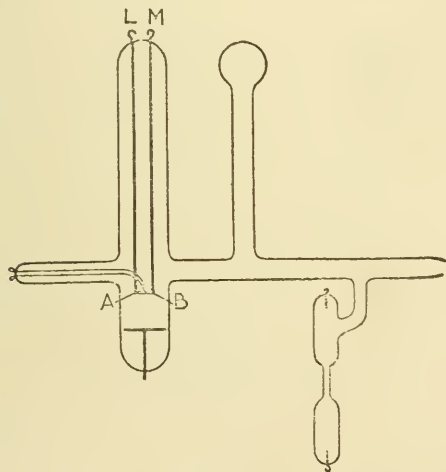


FIG. 1.

might be expected to throw some light on the very interesting question of the genesis of spectra. Many important points can very conveniently be studied by the aid of Wehnelt's method of producing the current. In this method the cathode is a strip of platinum or a piece of platinum-wire on which either a little lime or barium oxide has been deposited. This when heated to redness emits large supplies of corpuscles, and by altering the temperature of the platinum very large variations in the current passing through the tube and the potential difference between the electrodes can be obtained. In our experiments the current has varied from a small fraction of a milliampère to several amperes, and the potential difference from a few volts to several hundred.

The apparatus used is shown in Fig. 1. AB is the platinum strip with the lime on it; a thermo-couple, a platinum and platinum rhodium junction, was fused to this strip, and served to determine its temperature; the strip

was connected with the earth, and was heated by a current passing through the leads, LM; a rheostat was placed in series with the heating current, and by means of this the temperature could be altered gradually. The anode was a platinum disc; this was connected with the positive pole of a battery of storage cells, the negative pole of which was earthed; to allow of gradual variations in the potential difference between the electrodes a potential divider of 100 resistances of 10 ohms each was used. The current through the tube was measured by a D'Arsonval galvanometer, and the potential difference between the terminals by a Weston's volt-meter.

Some of the most interesting features of the discharge are very prominent when the temperature of the platinum is high, say, 1400°C ., and the pressure of the gas low, less than 0.01 m.m. of mercury. The discharge is light blue, and its spectrum shows the mercury lines and the band spectrum of nitrogen. In this case the relation between the current and the potential difference is represented by a curve like Fig. 2, the ordinates representing the current and the abscissæ the potential difference. G is the point at which the luminosity begins. In the case we are considering, when the wire is very hot and the pressure low, the change from the dark to the luminous discharge takes place very abruptly, an increase of the potential difference by $\frac{1}{100}$ th of a volt being often sufficient to convert a dis-

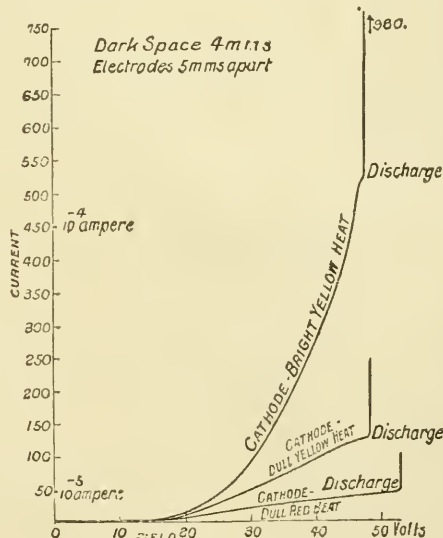


FIG. 2.

charge, where no light could be detected, even in a darkened room, to one where the light was quite bright. When luminosity appears, there is a very rapid increase in the current; in some of the experiments an increase in the potential difference of $\frac{1}{100}$ th of a volt increased the current forty-fold. At this stage the thermopile showed that there was no increase in the temperature of the platinum when the luminosity appeared. We shall see later on that it is possible by using large potential differences to get such large currents through the tube that the platinum becomes appreciably warmer by the passage of the current.

One point which I think very suggestive is the abruptness with which the luminosity round the cathode appears. We see that by a very small increase in the potential difference the discharge passes from a state in which no luminosity can be detected, even in a dark room, to one where the luminosity can plainly be seen in a bright light; thus the molecules of the gas in the tube just when the luminous discharge is on the point of appearing, are in a state

* A Discourse delivered at the Royal Institution, January 19, 1906.

in which a very small change in the electrical conditions of the tube make the molecules pass from a state in which they are not giving out an appreciable amount of light to one where they are brightly luminous; and, as the great increase of the current when the luminosity appears shows, this change in state is accompanied by an emission of corpuscles. From this and other considerations, I have come to the conclusion that what takes place when the gas becomes luminous is that the internal energy in the atom in consequence of its bombardment by the corpuscles increases, and when it gets up to a certain critical value the equilibrium of the atom becomes unstable; an explosion occurs, resulting in an expulsion of corpuscles and such a shaking up of those left in the atom that these vibrate so vigorously that the energy radiated is sufficient to produce luminosity. Thus, I regard the ionisation of the gas as being due, not to the corpuscles in the atom being dragged out by the direct action of the electric forces in the field, or as being knocked out by a rapidly moving corpuscle striking against them, but to an explosion due to the atom having absorbed so much internal energy that its equilibrium becomes unstable. Other phenomena point to this as the method by which ionisation is effected. If the corpuscles are dragged out of the atoms by the electric field, the velocity with which they are projected should depend upon the strength of the field; while, if they are projected by an explosion, their velocity would depend upon the nature of the atom and not upon the strength of the field. Now when Röntgen rays fall upon a substance, the atoms of the substance are ionised, and corpuscles, forming a stream of cathodic rays, are emitted. Barkla has lately shown, however, that the penetrating power of the cathodic rays produced in this way is independent of the intensity of the Röntgen rays. Now the electric force in the Röntgen rays depends upon their intensity, and the penetrating power of the cathodic rays depends upon their velocity; so that this result shows that the velocity of the corpuscles does not depend upon the intensity of the force acting upon them. Again, Lenard has shown that the velocity of the corpuscles ejected when ultra-violet light falls upon a metal is independent of the intensity of the light. Lenard also investigated the secondary cathode rays produced when cathode rays fall upon matter, and found that, in addition to rays, whose velocity was of the same order as that of the primary rays, and which may be regarded as deflected primary rays, there were other very slow rays; and the measurements he gives indicate that the velocity of these varies but little with that of the primary rays.

A point of great importance, which can easily be shown by this apparatus, is that the stage at which luminosity sets in depends upon the current density through the tube, and not merely upon the potential difference. One way of showing this is to lower the temperature of the platinum, keeping all the other conditions the same, and again determine the relation between the current and the potential difference. The effect of lowering the temperature is to reduce the number of corpuscles starting from the cathode, so that with the same potential difference the current density is smaller. If the relation between the current and potential difference are represented by curves, such as those in Fig. 3, it will be seen at once that the curve for the cooler electrode cannot be deduced from that for the hotter by reducing all the ordinates in the same proportion. The critical points on the curves, *i.e.*, the place where ionisation by collision begins and where the luminous discharge appears, are at very different potentials; the greater the current density the smaller the potential difference corresponding to these critical points. Thus, to take a case actually observed, when the wire was very hot the discharge was brightly luminous with a potential of 24 volts, but on lowering the temperature no luminosity could be detected with a potential difference of 110 volts.

We can also show the effect of current density without altering the temperature of the cathode, by placing near

the tube an electromagnet, so arranged that its lines of magnetic force in the discharge tube are along the line joining the cathode and the anode. The effect of the magnetic field is to make the corpuscles move along the lines of force, and thus, without altering the number of corpuscles emitted by the cathode, it concentrates their paths, and so increases the maximum current density in the tube. When the magnet is on, ionisation by collision and luminosity both occur at a much lower potential difference than when it is off, and it is easy to arrange matters so that keeping the potential difference constant, the discharge is luminous when the magnet is on and dark when it is off. When the potential difference is too small to produce a bright discharge even when the magnet is on, the current through the tube is often greater when the magnet is on than when it is off. By placing the magnet so that the lines of magnetic force are across the line joining the cathode to the anode, we can render the paths of the corpuscles more diffuse than they would be without the field, so that the maximum current density is less when the magnet is on than when it is off. In this case it requires a larger potential difference to produce a luminous discharge

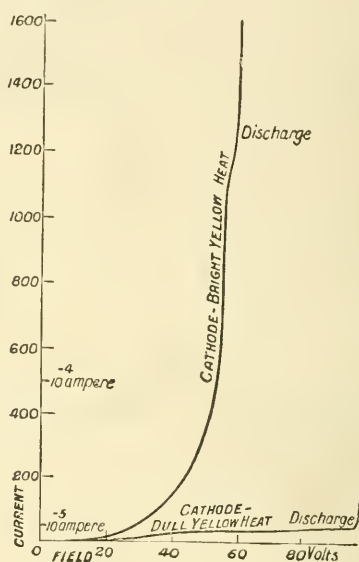


FIG. 3.

with the magnet on than with it off. Similar effects produced by a magnet on another kind of discharge are described in my "Recent Researches," p. 105.

The potential difference, *P*, just when the glow commences, when the pressure is low, sometimes varies so rapidly with the current *i* as to be roughly inversely proportional to it. The following are some values of *i* and *P* for a gas at a constant low pressure as the temperature of the platinum strip was increased. The numbers are in the order of increasing temperature:—

<i>i</i> (in scale divisions).	<i>P</i> (volts).	<i>Pi</i> .
6	60	360
8.7	40	348
11.2	30	336
14	25	350

Such a simple relation between *P* and *i* is, however, exceptional.

The fact that the potential differences at which ionisation by collision or luminosity begin depend upon the current density, shows that the ionisation or luminosity of an atom need not, and indeed cannot entirely, be the result

of a single collision between a corpuscle and the atom. For if that were the case, then, since the energy of the corpuscle depends only upon the electric field and not upon the current density, the effect of increasing the current density would merely be to increase in the same proportion the number of luminous atoms, while, as a matter of fact, if the potential difference is kept constant and the current increased by raising the temperature of the platinum strip, the increase in the luminosity is greater out of all proportion than the increase in the strength of the current.

The result, however, is easily explained if we look at the question from the following point of view:—Suppose that for ionisation or luminosity to take place the internal energy of the atom must increase by certain amounts, say, E_1 , E_2 respectively. Then, if the energy possessed by the corpuscle were very great, the result of one collision with an atom might be to give to the atom enough energy to ionise it or make it luminous, or both. But even if the corpuscle were less energetic, and did not in one collision give enough internal energy to the atom to ionise it, it would communicate some energy to it, and if the atom had any power of storing up energy, this would form a contribution towards the critical amount of energy required by the atom before it is ionised. The atom, after having had this energy communicated to it, would not, as long as it retained any of it, require so much energy to ionise it as before. The atom, too, might acquire energy, not merely by corpuscles striking against itself, but also by the collision of corpuscles with neighbouring atoms. Such collisions generate soft Röntgen rays, the energy of which might be absorbed by the atom under consideration, and help to raise its energy to the critical point. The energy in the Röntgen rays might by itself raise the internal energy of the atom to this value, or else raise it so nearly to this value that the collision with a corpuscle would give it enough energy to carry it past the critical stage. The rate at which the energy, due to collisions of corpuscles with itself or with neighbouring atoms, comes to an atom will be proportional to the rate at which energy is being communicated to the gas, i.e., to $F \times i$, where F is the electric force and i the current density; and thus for a constant electric force would be proportional to the current density. The atom will radiate away some of its internal energy; if the rate of this radiation is proportional to the amount of energy E possessed by the atom, say, equal to βE , then if q is the rate at which energy is being communicated to the atom, we have—

$$\frac{dE}{dt} = q - \beta E,$$

so, if E vanishes with t ,—

$$E = \frac{q}{\beta} (1 - e^{-\beta t}).$$

Thus, q/β is the limit to the energy acquired by the atom, and this is proportional to q , while q is proportional to $F i$; so that the atom will acquire the critical amount of energy, or not, according as $F i$ is greater or less than a certain value.

(To be continued).

THE GERMICIDAL ACTION OF POTASSIUM PERMANGANATE.

(INTRODUCTORY PAPER).

By JAMES B. GARNER and WALTER E. KING.

THE use of solutions of potassium permanganate as a disinfecting agent has been extensive and popular, from the standpoint of both efficiency and economy. Accurate details regarding the antiseptic and germicidal action of potassium permanganate upon *B. typhosus* seem to be lacking. Jäger's and Miquel's statements are only

approximate ones (Sternberg's "Bacteriology," p. 186). Jäger says that a 5 per cent solution (approximately N/1.6) of potassium permanganate is a germicide to all pathogenic organisms, excepting tubercle bacillus, and that a 1 per cent solution (approximately N/0.32) is not reliable for the destruction of these same organisms. According to Miquel, potassium permanganate is an antiseptic in the proportion of 1 : 285 (approximately N/0.091).

Our preliminary experiments, made upon a pure 24-hour bouillon culture of *Bacillus typhosus*, with dilute solutions of potassium permanganate, lead us to believe that the reagent is antiseptic and germicidal in less quantities than those given by Miquel and Jäger. The results of these preliminary experiments, therefore, occasioned the work of this introductory paper on the general subject of the germicidal action of potassium permanganate. We purpose to study closely the action of solutions of this reagent upon all of the common pathogenic organisms.

Methods.

In conducting the experiments all apparatus, including pipettes, burettes, test-tubes, flasks, graduates, &c., was sterilised, and all possible precautions were observed to avoid contamination. One-half litre quantities of sterile distilled water, in sterile glass flasks, were used in the eight series. Each series consisted of two flasks of sterile water, to each of which 1 c.c. of a pure 24-hour bouillon culture of *B. typhosus* was added, thus affording a means of checking results. Varying volumes of N/6000, N/4000, N/1000, and N/10 solutions of potassium permanganate were added to the several flasks containing the water and culture. The mixtures were incubated, and, after varying periods of incubation, the ordinary methods were followed to determine the presence or absence of organisms.

Experimental Part.

In each of the two flasks of the eight series given below, 500 c.c. of sterile distilled water were used, varying amounts of potassium permanganate solutions were added, as indicated for the different series, then 1 c.c. of a pure 24-hour bouillon culture of *B. typhosus*, excepting in Series V. The temperature of the incubation was 37.4° and the periods of growth were from twenty-four to seventy-two hours:—

Series I.—Flasks *a* and *b*, 25 c.c. N/6000 potassium permanganate were added. Total volume, 526 c.c.

Series II.—Flasks *a* and *b*, 20 c.c. N/4000 potassium permanganate were added. Total volume, 521 c.c.

Series III.—Flasks *a* and *b*, 20 c.c. N/1000 potassium permanganate were added. Total volume, 521 c.c.

Series IV.—Flasks *a* and *b*, 10 c.c. N/10 potassium permanganate were added. Total volume, 511 c.c.

Series V.—Flasks *a* and *b*, no potassium permanganate added. Check flasks. Total volume, 501 c.c.

Series VI.—Flasks *a* and *b*, 25 c.c. N/6000 and 12.6 c.c. N/10 potassium permanganate solutions were added. Total volume, 538.6 c.c.

Series VII.—Flasks *a* and *b*, 20 c.c. N/4000 and 20.1 c.c. N/10 potassium permanganate solutions were added. Total volume, 541.1 c.c.

Series VIII.—Flasks *a* and *b*, 20 c.c. N/1000 and 50.3 c.c. N/10 potassium permanganate solutions were added. Total volume, 571.3 c.c.

After all the flasks had remained in the incubator for twenty-four hours, tubes of sterile bouillon, 15 c.c. each, were inoculated with 1 c.c. from each flask. These bouillon tubes were incubated for twenty-four hours; cloudy growth was noted in all tubes of Series I., II., III., and V.; slower growth was shown, however, in the tubes inoculated with samples from Series IV., *a* and *b*, and not until the end of thirty-three hours' incubation did these tubes show a uniform cloudy growth. Tubes from Series VI., VII., and VIII. remained clear after forty-eight and seventy-two hours' incubation. Three repetitions of these inoculations gave the same results.

Tabulation of Results,

Series.	Volume of permanganate. C.c.	Total volume. C.c.	Concentration of permanganate.	Growth checked.
I., a and b	25 N/6000	526	N/126260	—
II., a and b	20 N/4000	521	N/104200	—
III., a and b	20 N/1000	521	N/26050	—
IV., a and b	10 N/10	511	N/511	(a)
V., a and b	None	501		(b)
VI., a and b	25 N/6000	538.6	N/426.6	+
	12.6 N/10			
VII., a and b	20 N/4000	541.1	N/213.35	+
	20.1 N/10			
VIII., a and b	20 N/1000	571.3	N/113.06	+
	50.3 N/10			

(a) Growth inhibited, 67 colonies per c.c.

(b) Check flasks, 4050 colonies per c.c.

Agar plates were inoculated with 1 c.c. from Flask a, Series IV. After forty-eight hours' incubation the average colony count showed 67 per c.c.

An agar plate was inoculated with 1 c.c. from Flask a, Series V. After thirty-two hours' incubation 4050 colonies per c.c. were estimated.

In the above experiments all cultures were studied in regard to morphology and cultural characters, and no contaminations were observed.

The results obtained from the flasks of Series IV. indicate that N 511 potassium permanganate is antiseptic to *B. typhosus*.

The mixtures in the flasks resulting from experiments, Series VI. to VIII. inclusive, were of a rose colour, thus indicating an excess of permanganate. An excess of 0.00245 gm. permanganate was found in Flasks a and b of Series VI., by titration with standard ferrous ammonium sulphate solution in presence of dilute sulphuric acid. This excess, deducted from the total quantity added, left the amount of permanganate which was germicidal to *B. typhosus*. The concentration calculated is N/458.—*American Chemical Journal*, xxxv., No. 2.

ON THE COMPOSITION OF PETROLEUM.*

THE SULPHUR COMPOUNDS AND UNSATURATED HYDROCARBONS IN CANADIAN PETROLEUM.

By CHARLES F. MABERY and WILLIAM O. QUAYLE.

(Concluded from p. 194).

Unsaturated Hydrocarbons of the Series C_nH_{2n} .

THE need of more accurate information concerning the presence of hydrocarbons of the ethylene series, C_nH_{2n} , in petroleum, was explained in a former paper of this series. Notwithstanding persistent attempts in the numerous treatises on petroleum to show that these bodies have been identified, a critical examination of published results fails to reveal adequate proof of sufficient foundation for these statements. The statement in "Petroleum and its Products," by Redwood, that De la Rue and Mueller proved the presence, in preponderant quantities, of the ethylene group in Rangoon petroleum is not supported by the results, nor by the conclusions of those authors. Concerning the results of Warren, Schorlemmer, and Chandler, it is not true, as asserted by Redwood, that those chemists found the ethylene series in Pennsylvania petroleum. There are no allusions to this series in Schorlemmer's published papers.

Beyond adopting the general nomenclature then accepted for the ethylene series, Warren evidently left it an open

question as to what should be the structural formulae of the products he separated from Pennsylvania petroleum. There are no statements in his papers to show that he made any further preparation of his products for analysis than boiling with sodium, and no further examination to prove structural forms. Certainly it would have been easy to demonstrate the unsaturated condition of those bodies had they contained doubly bonded carbon, and in view of Warren's clear-sighted and painstaking methods, he could not have overlooked the importance of those tests. In none of his papers on Pennsylvania petroleum does the term olefine or ethylene appear.

The assertion of Hoefer that members of the olefine series, C_2H_4 to $C_{30}H_{60}$, have been found in American petroleum, has no foundation. In fact, besides the investigations within recent years in this laboratory leading to a better knowledge of the various series of hydrocarbons with high boiling-points, no attempts have been made to discover the true composition of American petroleum. In fractions below 200° from Galician oil, Lachowicz obtained no reaction with bromine, yet, so far as they have been examined in this laboratory, distillates below 200° from American oils do not fail to show a considerable bromine absorption. The sulphur compounds in Ohio and Canadian oils have a great affinity for bromine. Substitution may take place in the aromatic hydrocarbons which American oils contain, as well as in the hydrocarbons C_nH_{2n+2} , unless light is excluded. All these bodies, and probably others, are affected in the ordinary determinations of bromine absorption.

At the suggestion of one of us, (C. F. M.), in connection with another line of work on petroleum, Mr. T. A. Hicks, a student in this laboratory, undertook a study of bromine absorption in crude oil and in fractions obtained from it after various modes of treatment. Two determinations in the oil before treatment gave, as the percentage of bromine absorbed, (I.) 8.43 and (II.) 8.73. A portion agitated with alcoholic mercuric chloride, washed, and dried, gave (I.) 9.27 and (II.) 9.58, indicating that the crude oil holds in solution, to some extent, the mercuric chloride compound. After treatment with mercuric chloride, a portion of the oil shaken with common concentrated sulphuric acid gave with bromine (I.) 5.91 and (II.) 5.94. The oil was next shaken with fuming sulphuric acid, washed, and dried, when it absorbed bromine equivalent to (I.) 3.47 and (II.) 3.72. A portion of the oil, after the last treatment, was distilled under atmospheric pressure, fractions collected at 100—125°, 125—200°, and 200—230°. In the first distillate the bromine absorption was:—(I.) 4.65, (II.) 4.75; in the second (I.) 4.63, (II.) 4.58; and in the third (I.) 5.61, (II.) 5.17 per cent. Another portion of the treated oil was distilled under 50 m.m., collecting at 130—160°, 160—190°, 190—260°, and a residue, and the bromine absorption determined. Bromine absorption gave in the first distillate (I.) 1.73, (II.) 2.00; in the second (I.) 1.96, (II.) 2.01; in the third (I.) 3.28, (II.) 3.15; and in the residue 9.52. From these results it is evident that substitution in the less volatile portions of the crude oil or cracking has much to do with the amount of bromine absorbed, especially since, in these experiments, the reagents employed for the removal of the sulphur compounds should also remove unsaturated hydrocarbons. In this connection Mr. Hicks determined bromine absorption in some distillates from Pennsylvania, Ohio, and Canadian oils, that has been especially purified by long distillation and treatment with reagents, as has been more fully described in another paper. A distillate, 194—196°, from Pennsylvania petroleum, gave 0.02 per cent bromine absorbed; another, 209—210°, 0.09 per cent; a distillate 209—210° Ohio, purified in the same manner, gave 0.03 per cent bromine, and a Canadian distillate, 0.12 per cent. These results may be accepted as showing no absorption of bromine, since this method is not capable of indicating such small percentages. That the quantity of sulphur remaining in the crude oil, after treating with fuming sulphuric acid, was too small to affect the amount of bromine absorbed, is shown by the low

* Contributions from the Chemical Laboratory of Case School of Applied Science. From the *American Chemical Journal*, xxxv., No. 5.

percentage of sulphur, 0.09, and in the distillate 200—230°, atmospheric pressure, 0.001 per cent.

When the complex composition of American petroleum is borne in mind, and the probability of substitution in the less volatile portions, the difficulties in testing for unsaturated hydrocarbons are evident. Consequently, all discussion of this subject by those best informed has been undertaken with reservation, while those of others partake more of the nature of speculation on results which the authors were content merely with presenting, without attempting explanations which the facts were insufficient to justify.

We have had good evidence that unsaturated hydrocarbons are contained in distillates prepared from crude petroleum. Polymerisation on standing, the formation of dark coloured heavy oils can only be explained by changes in unsaturated hydrocarbons or unsaturated sulphides. Heptylene was described in another paper as a constituent of Ohio oil.

Since the products described in this paper were contained in the oil extracted with sulphuric acid from burning oil distillate, we have assured ourselves, by experiments already described, that ordinary concentrated sulphuric acid, such as is used in refining burning oil distillates, removes from such distillates, without decomposition, the unsaturated hydrocarbons as well as the sulphur compounds, and, consequently, that the sludge oil, after carefully separating from the acid, contained constituents of the crude oil and not products of decomposition.

In fractioning *in vacuo*, as previously explained, a considerable proportion of the distillates from the sludge oil collected below 100°, which could be distilled without decomposition under atmospheric pressure. These portions were therefore carried through ten distillations under atmospheric pressure, and the portions distilling below 150° *in vacuo* also through ten additional separations *in vacuo*. On account of great pressure of other work, these distillates stood three years before their study was resumed, although when first obtained they received sufficient attention to show that they contained unsaturated hydrocarbons (*Am. Chem. Journ.*, xvi., 92).

Upon returning to these distillates, it was found that some of them had undergone a marked change. Those collected at certain temperatures—especially at 44—45°, seventh distillation (50 m.m.); 70—71°, twenty-second distillation (atmospheric pressure); 97—98, tenth distillation (atmospheric pressure); 118—119°, tenth distillation (atmospheric pressure)—corresponding, in part, to the boiling-points of well-known hydrocarbons of the ethylene series, C_nH_{2n} , had deposited heavy dark red oils in considerable quantities, evidently products of polymerisation. Some of the polymerised oils were found to contain as much as 8 per cent of sulphur, although polymerisation took place in oils containing not more than 1.5 per cent of sulphur. It was interesting to observe that distillates on either side of those from which the heavy oils separated remained unchanged and were scarcely more discoloured than when they were first distilled. That the distillates below 150° contain sulphur compounds with a peculiar odour, attacking the eyes, and in other respects different from the series $C_nH_{2n}S$ described above, has been apparent since the first distillation of these oils, although these peculiar compounds are evidently present in much smaller proportions than the others.

All these fractions, as well as those above 150°, united with bromine with explosive violence, and with the evolution of great heat. The bromine addition products, however, were found to be so unstable that it was impossible to purify them by distillation even *in vacuo*. They decompose rapidly, even on standing, with the separation of hydrobromic acid. In ascertaining the composition of these hydrocarbons we have therefore relied on the more stable addition product obtained with hydrobromic acid, which had the further advantage that having no action on the sulphur compounds, the latter need not be removed before heating with the acid.

Hexylene.

For the identification of hexylene, the small quantity of the fractions 70—80°, twenty-second distillation (atmospheric pressure), were put together, and a portion was heated to 120°, during five hours, with fuming hydrobromic acid. The product was washed, dried, and fractioned *in vacuo*. On account of the higher boiling-point of the bromide it was easy to separate the addition product, and of the small quantity obtained the greater portion collected at 62—65° (50 m.m.). The boiling-point of the bromide under atmospheric pressure could not be determined on account of its instability, but it probably was not far from 135°. The distillate selected for the formation of this bromide was nearly the same in boiling-point as that of the hexylenes from various sources, 65—70°. Upon analysis values were obtained corresponding to those required for monobromhexane:—

I. 0.1938 grm. oil gave 0.3108 grm. CO_2 and 0.128 grm. H_2O .

II. 0.2720 grm. oil gave 0.3045 grm. AgBr.

	Calculated for $C_6H_{12}Br$.	Found.	
		I.	II.
C	43.63	48.73	—
H	7.88	7.41	—
Br	48.51	—	47.64

On account of the small amount of this substance it was not possible to purify it more completely.

Heptylene.

The fractions 98—102°, tenth distillation (atmospheric pressure), more nearly corresponding to the boiling-points of the various heptylenes, 90—100°, were selected especially because they contained a considerable quantity of the polymerised oil. On either side of these limits the distillates had not changed. After treatment with fuming hydrobromic acid and fractioning *in vacuo*, the greater portion of the bromide collected at 76—80° (50 m.m.). It could not be distilled under atmospheric pressure, but its boiling-point was probably not far from 160°. The results of analysis corresponded to the composition of monobromheptane:—

I. 0.2000 grm. oil gave 0.3498 grm. CO_2 and 0.1592 grm. H_2O .

II. 0.2117 grm. oil gave 0.2188 grm. AgBr.

	Calculated for $C_7H_{14}Br$.	Found.	
		I.	II.
C	46.97	47.71	—
H	8.38	8.90	—
Br	44.73	—	43.99

The sp. gr. of this heptyl bromide was found to be 1.1601.

Octylene.

Octylene was sought for in the fraction 118—119°, tenth distillation (atmospheric pressure), from which had separated a small quantity of the heavy polymerised oil. After heating with concentrated hydrobromic acid the oil was fractioned *in vacuo* until 15 grms. collected at 93—95° (50 m.m.), corresponding, approximately, to 180°, atmospheric pressure. The boiling-point of the distillate selected is near that of di-isopropyl ethylene, 116—120°, and also that of the octylene, 115—117°, prepared from octylene chloride by Schorlemmer.

Analyses of the bromide gave values required for monobromoctane:—

I. 0.1941 grm. oil gave 0.3486 grm. CO_2 and 0.1613 grm. H_2O .

II. 0.1885 grm. oil gave 0.1851 grm. AgBr.

	Calculated for $C_8H_{17}Br$.	Found.	
		I.	II.
C	49.71	49.00	—
H	8.81	9.23	—
Br	41.45	—	41.83

The sp. gr. of this octyl bromide was found to be 1.1836.

Nonylene.

The fraction 140—141°, tenth distillation (atmospheric pressure) was selected for the addition of hydrobromic acid. In fractionating the bromide *in vacuo*, after the separation of the portion not affected by the acid, the temperature rapidly rose to 110°, and more of the distillate collected at 110—113° than at any other point in this vicinity. This product was less stable than the lower homologues, but its boiling-point under atmospheric pressure would probably be in the vicinity of 200°. Upon analysis it gave values required for bromononane:—

- I. 0.1798 grm. oil gave 0.3481 grm. CO_2 and 0.1501 grm. H_2O .
- II. 0.2117 grm. oil gave 0.1888 grm. AgBr.

	Calculated for $C_9H_{19}Br$.	Found.	
		I.	II.
C	52.17	52.80	—
H	9.18	9.33	—
Br	38.65	—	37.96

The sp. gr. of this bromononane was 1.2084.

Higher fractions failed to give us addition products with hydrobromic acid, either because the additive power of the hydrocarbon was too weak, or because, if the addition product were formed, it was decomposed by distillation *in vacuo*. The first explanation is probably correct, since we have never noticed the evolution of hydrobromic acid in any considerable quantity. Perhaps it is more reasonable to assume that our distillates contained no higher homologues of this series than those that were identified.

With reference to the solvent power of sulphuric acid for the hydrocarbons described above, it is doubtless true that compounds with this acid of the hydrocarbons with high molecular weights are less stable, and partake more of the nature of mechanical solution. It is doubtless also true that the mechanical solvent power of the acid is increased by the other oils that the acid dissolves. If the acid solution separated from the oil be neutralised with calcium hydroxide, certain lime salts are formed, crystallising in long needles, and consisting, at least in part, of nitrogen bases, but sulphonates of the ethylene hydrocarbons and of allied series have not been observed. That unsaturated hydrocarbons may be extracted by sulphuric acid and precipitated by dilution, has been shown in several experiments. We diluted a carboy of sludge acid by pouring slowly into water, and found the precipitated oils to contain these hydrocarbons. As to their relative proportion in the crude oil we have no precise data, but in comparison with the principal constituents it is extremely small.

Since the sulphur compounds described in this paper, as well as the alkyl sulphides, are also readily soluble in sulphuric acid, they should be removed as a part of the sludge in refining burning oil distillates.

The results described in this paper may be summarised as follows:—The separation from Canadian petroleum of the following series of sulphur compounds: Hexyl, heptyl, octyl, nonyl, decyl, undecyl, quaterdecyl, sexdecyl, octodecyl thiophanes; the formation of corresponding sulphones by oxidation.

Canadian petroleum contains, in minute proportions, unsaturated hydrocarbons, $C_{H_{2n}}$, apparently of the ethylene series. Canadian petroleum contains certain sulphur-free oils soluble in alcohol, and different in odour and in other respects from the series hitherto identified in petroleum, possibly terpenes.

We desire to acknowledge our obligations to Messrs. C. A. Lattimer and R. C. McBride for assistance in the purification and analysis of the sulphur compounds.

NOTES ON TYPEWRITER RIBBONS.

By A. M. DOYLE.

It is only within comparatively recent years that typewriter machines have been perfected so as to be of practical use. The advantages of such a mechanical contrivance were so great, however, that they were quickly recognised by business men, and the use of the machine has to-day become so general that it has almost completely replaced the old style of longhand writing. Naturally questions have arisen as to the character of the records made, especially as regards permanence. This question was investigated in 1890 by Mr. Thomas Antisell, Chemist of the U.S. Patent Office, his results being published in the report of the Commissioner of Public Records of the State of Massachusetts. Other than this report, the writer has been unable to find any literature on the subject of typewriter ribbons.

The Bureau of Chemistry has received requests for information in regard to the character of records made by typewriter ribbons, and these, as well as the need for data to guide in the awarding of contracts, have led the Contracts Laboratory to make the following investigation. The writer is indebted to Mr. L. S. Munson, Chief of the Contracts Laboratory, for many valuable suggestions that were of assistance throughout the work.

Samples were obtained from the Supply Divisions of the various departments and from operators in the Department of Agriculture. The total number of ninety-nine ribbons included fifty-nine new and forty old ribbons, representing forty-three brands and nineteen manufacturers. There were 31 record ribbons (mainly black record), and 68 copy ribbons, among which were 30 indelible copy, 11 black copy blue, 12 blue copy, 11 purple copy, and 4 of other kinds.

Operators sending samples of old ribbons were asked to state the length and quality of service rendered by the ribbon, and in this manner information was gathered from a large number of workers. Complaint was made that the ink gummed or smeared; that there was too much ink, clogging the type and making frequent cleaning necessary; that, on the other hand, some ribbons contained an insufficient amount of ink, and therefore did not clog the type, but were not enduring; that ribbons were unevenly inked, giving spotted writing; that the writing of some ribbons, notably that of the purple copy, faded readily, and that the fabric forming the basis of the ribbon wrinkled and stretched along the edges and wore badly in holes.

The length of service as reported varied from less than three weeks to more than seven months, the general idea being that a ribbon should last from six to eight weeks. Very much depends, however, upon the touch of the operator and the action of the machine, as well as the use for which the writing is intended. The amount written by one ribbon was variously reported to be from 264 pages to 2100 pages; the number of words was estimated to be from 109,000 to 630,000, which shows that great differences exist, not only in the amount of work done, but in the methods of estimating it.

The work of the investigation was conducted along three general lines:—

1. Tests to show the quality of the ribbon fabric—width, total length, weight per square centimetre inked and clean, tensile strength, number of threads in warp and woof, and the metric yarn number.
2. Tests to ascertain the nature of the ink—moisture, ash, lampblack, dye, oil, total inking material and clean ribbon, determining the kind and quantity of each.
3. Rating of writing and copy on a scale of ten, and the action of reagents on the written matter by exposure to sunlight, water, 10 per cent ammonia, 2 per cent hydrochloric acid, two-hundredth-normal bleaching powder.

1. Tests of Fabric.

In the accompanying summary (Table I.), the figures were taken from a detailed tabular statement, and show the average

TABLE I.

Kind of test.	Kind of ribbon.	Number of samples.	Unit of measure.	Variation.	Average.
<i>New Ribbons.</i>					
Width	Wide	61	C.m.	3'4—3'8	—
	Medium . . .	7		2'4—2'6	—
	Narrow . . .	31		1'0—1'2	—
Total length	Wide	68	Feet	19'00—28'50	25'50
	Narrow . . .	31		29'50—54'50	42'80
Weight, sq. cm., inked . .	Record . . .	20	M.grm.	8'50—11'76	9'80
	Copy	39		7'26—11'68	9'49
Weight, sq. cm., clean . .	Record . . .	20	M.grm.	5'58—8'76	6'47
	Copy	39		4'79—7'62	6'15
Tensile strength	Wide	35	Pounds	26'50—50'30	38'80
	Narrow . . .	20		11'70—27'80	20'60
Number of threads	Wide	48	—	48 × 43—58 × 56	54 × 52
	Narrow . . .	28	—	50 × 49—63 × 47	59 × 45
Metric yarn number . . .	Wide	48	—	50—105	85
	Narrow . . .	28	—	65—110	85
<i>Old Ribbons.</i>					
Weight, sq. cm., inked . .	Record . . .	11	M.grm.	8'21—11'37	10'11
	Copy	29		7'55—11'47	9'42
Weight, sq. cm., clean . .	Record . . .	11	M.grm.	5'88—8'59	7'61
	Copy	29		4'89—8'23	6'62
Tensile strength	Wide	14	Pounds	16'50—39'10	27'10
	Narrow . . .	6		11'50—22'70	19'50

TABLE II.

Number of samples from one manufacturer.	Variation, inked ribbon.	Per cent.	Variation, clean ribbon.	Per cent.	Average.	
					Inked.	Clean.
31	7'97—10'02	23	4'93—6'29	23	8'92	5'90
16	8'51—11'68	30	6'08—8'23	30	10'63	7'17
12	8'98—10'74	18	6'18—7'90	25	9'86	6'93
11	8'50—10'75	24	4'96—6'18	21	9'26	5'72

TABLE III.

Kind of test.	Number of samples.		Variation, both new and old (per cent).	Average (per cent).		
	New.	Old.		New.	Old.	Total.
Moisture, or matter volatile at 100° C. . .	59	40	2'67—6'06	4'28	3'68	4'05
Ash	58	22	0'43—15'24	2'48	1'82	2'27
Lampblack, record	18	8	0'88—7'00	3'18	2'32	3'03
Lampblack, copy	22	18	0'25—3'44	1'57	1'54	1'56
Dye	31	—	3'34—9'26	5'85	—	5'85
Oil	59	22	15'43—31'02	22'09	19'40	21'26
Total ink	58	40	20'56—46'00	34'78	28'42	33'38
Clean ribbon	58	40	79'44—54'00	65'22	71'58	66'62

for each test, as well as the variation. The figures for old ribbons in width, length, number of threads, and yarn number were about the same as for new ribbons, and were therefore included among them.

The varying widths of ribbons adapt them for use on different machines. In all totals, medium width ribbons were included among wide ribbons. In length, wide ribbons varied from 19 feet to one-half as much more, and narrow ones ranged from 29 feet to nearly twice the amount, the averages being 25'5 and 42'8 feet respectively.

Considering the weight per square centimetre, the weight of the inked ribbons, both new and old, varied as much as one-third of the average weight; the weight of the clean ribbons varied as much as one-half of the average weight; and these variations were as much or greater than the total amount of the ink found by taking the difference between the totals for inked and clean ribbons—that is, the average weight of ink was found to be about one-third the weight of the ribbon, and the variation among different ribbons equalled or even exceeded the weight of ink. The average weight of the inked ribbon differed very little whether the

ribbon was old or new. The averages for 59 new and 22 old ribbons, eliminating certain abnormal figures which appear in the above totals, were 9'60 and 9'34 m.grms. per sq. c.m. respectively. Inasmuch as all of the old ribbons were reported by operators to be in an exhausted condition, it would appear that the exhaustion of a ribbon depends more upon the wear of the fabric than upon the amount of ink removed. In connection with the weight per square centimetre, the evenness of the inking was tested by comparing the weights of ten or more sections of the same ribbon. The strips, which were about 35 c.m. long, weighed approximately 1 grm., and were found to vary as much as 10 per cent of the average weight. Shorter lengths would probably have shown greater differences.

Table II. shows the variation and averages of the weights per square centimetre for the products of the same factory.

The variation, calculated on the average weight, ranged in the inked ribbon from 18 to 30 per cent, and in the clean ribbon from 21 to 30 per cent. The variation for clean ribbon, therefore, was equal to or greater than that for the

inked ribbon, which would seem to show that the ribbon fabric varies rather than the quantity of ink. In the last line, where an exception may be noted, the eleven samples were obtained at the same time from the manufacturer, and there was noticeably less variation in the strength of the material as determined by the tensile strength tests. It is possible, therefore, that a part of the variation may be due to the varying ages of the ribbons, but, aside from this, it is evident that the weight of the material employed by manufacturers is far from being uniform.

The figures for tensile strength represent each an average of at least ten, frequently twelve or fifteen determinations. One inch of the ribbon was tested at a time, and so great were the differences between sections that a fair average was obtained only by a large number of tests. Many of the ribbons showed differences of as much as $7\frac{1}{2}$ pounds in successive tests on the same ribbon, while the maximum difference for the same ribbon was 12 pounds. Comparing different ribbons, some bore fully twice the strain of others in the same class. Old ribbons, as might be expected, were of less strength, the total difference being marked in the case of wide ribbons, but obscured in the total for narrow ribbons because of the presence of selvage.

The number of threads, warp and woof, and the metric yarn number were ascertained by Mr. B. J. Howard, Chief of the Microscopic Laboratory. The number of threads, which were directly counted under a microscope with micrometer attachment, together with the weight per square centimetre of the clean ribbon, gave the yarn number, according to a formula worked out by Herzfeld (see "Yarns and Textile Fabrics"). The number of threads, yarn number, and tensile strength would naturally be closely related, but the results did not establish such relation, possibly because the date of manufacture was not considered. Ribbons may become weak and even fall to pieces in time, owing to the presence of corrosive materials in the ink, and it is therefore probable that the apparent lack of agreement in the three sets of figures is due to the fact that the ribbons had been on hand for a greater or less length of time.

2. Tests of Ink.

In the summary of the tests for the ink (Table III.), the averages for the new and old ribbons were separated, but the variation differences were not great enough to make two statements necessary. In all of the tests the variation among ribbons, both new and old, was very wide. The volatile matter, determined by heating to constant weight at 100°C ., averaged about six-tenths lower in old ribbons, showed practically no variation from day to day, but lessened gradually as the ribbon aged. The ash, which was determined by burning off carbonaceous matter at a low red heat, varied in general between 1 and 2 per cent. From 3 to 5 per cent is a high ash content, and above 5 per cent is very unusual. The kind and quantity of ash give valuable indications of the colouring matter used for the ink.

The determination of the lampblack was very difficult because it was almost impossible to separate it from the fibres of the ribbon. Of the several methods tried but two gave any measure of success, and these agreed only within two or three-tenths of a per cent. In one method the cotton material was dissolved away by strong sulphuric acid, and the resulting solution passed through a Gooch filter which retained the lampblack. The other method consisted in separating the lampblack mechanically in ethereal and alcoholic solution by shaking and rubbing, the carbon being collected on a Gooch crucible. The latter method allowed of a direct weighing of the cotton skeleton of the ribbon, and for this reason was the preferred method. All of the black record, black-copy-blue, and indelible copy ribbons contained lampblack, copy ribbons averaging about 1.5 per cent, and record ribbons about twice as much.

On treating the ribbon with ether to extract the oil and filtering through a Gooch crucible, it frequently happened

that the dye as well as the carbon was filtered out. After removal of all of the oil by ether, the ribbon and crucible were both dried and weighed. They were then treated with alcohol and water, and sometimes strong acid, which removed the dye, and, after drying and again weighing, the dye was found by difference. This method gave excellent results. Methylene blue, which was very commonly used, was determined by titration with a standard solution of Krystal Ponceau, according to a method worked out by E. Pelet and V. Garuti, published in the *Bulletin de la Soc. Chim. de Paris*. Duplicate tests agreed within 0.05 per cent. The summary gives the results of 31 determinations of methylene blue made by this method.

The oil was determined by extraction with ether and direct weighing. The amount of oil, which appears to influence the working qualities materially, averaged about 22 per cent. Much less shortens the life of the ribbon, and much more clogs the type and makes the writing blurred, while the length of service is not correspondingly increased.

The figures for total writing material equal the difference between 100 per cent and the total clean ribbon. Not a very close relation seems to exist between total ink and ribbon efficiency, although as a rule those ribbons having high working qualities possessed more than the average amount of ink, made up of more than average content of oil and dye. The total ink of ribbons of a popular make ranged from 27 to 38 per cent, showing that wide variation is possible in ribbons giving general satisfaction. Ribbons of much less than average ink may possess good working qualities for a time but they do not last well. Those with low percentage of either dye or oil seldom work well and low amounts of lampblack detract from the permanence of the writing. The percentage of available ink was roughly determined by taking short pieces of the ribbons, weighing, using to the point of exhaustion, and again weighing. Of the 27 ribbons thus treated, the loss ranged from 1.8 per cent to 16.5 per cent, with an average of 8.0 per cent calculated on the actual space exhausted. This agrees very well with an average loss of about 6 per cent of the total ribbon, shown in the summary of tests. The ribbons yielding the greatest amount of available ink, in the above test, did not as a rule give a larger amount of writing, but rather showed a tendency to clog the type and blur the writing, showing that the ink flowed too freely. One ribbon wrote twice the number of lines that any other ribbon was able to do, and contained 13.5 per cent of available ink. This ribbon contained high percentages of moisture and of dye, but only average amounts of the other ingredients. It is to be regretted that but one of this make of ribbon was examined.

3. Tests of Writing.

In the rating of the writing and the copy, the best was assumed as a standard, ranked one, and the other figures up to ten show a gradation from clear, strong impressions to writing that is barely legible. The effect of reagents was also rated on a scale of ten, ranging from one, or "unaffected" to ten, or "completely effaced." In all of the tests the uncopied writing, the copied writing, and the copy were similarly treated. The sunlight test, which was very severe, consisted in exposing the three kinds of writing, under glass, to the direct rays of the sun for ten days. Very weak solutions of the wet reagents were employed, but these, too, proved to be rather severe when applied for twenty-four hours. In a general way it was found that in treatment with reagents the original writing was severely attacked, the copied writing was less so, and the copy was completely effaced. With few exceptions record ribbons furnished permanent records, and the original writing of those copy ribbons that contained lampblack was permanent, but the copies were not. Copy ribbons failed to give indelible copies because almost none of the carbon was transferred. On exposure of the copy to sunlight for ten days or less, the dye faded out completely,

leaving the writing illegible. Most of the ribbons were very satisfactory when fresh, both the original and the press copy being good, but marked differences in the quality of the records were developed by wear, a number which gave good results at first being quickly exhausted.

From the foregoing it may be seen that ribbons of different makes differ widely in their properties; that ribbons of the same make differ as widely; that the ribbon itself is of uneven construction; that the fabric, more than the ink, is the cause of these variations; that many record ribbons furnish permanent records, and that much is yet to be desired in the attainment of truly indelible copy ribbons. It is evident that there is need for definite requirements to regulate the purchase of type-writer ribbons, especially as regards the material which is employed as a basis for the ink. An essential of a good ribbon is that the fabric be of the quality best fitted to endure the special kind of service required until all ink available for good writing is exhausted.—*Journal of the American Chemical Society*, xxviii., No. 6.

MEMORANDUM ON DRY CLEANING.*

IN 1896 a Departmental Committee reported upon the precautions necessary for the safety of persons employed in the process of dry cleaning. The recommendations of the Committee have been largely adopted, with satisfactory results, but accidents of a severe and sometimes fatal character are still reported from time to time. In the light of further experience it is now possible to suggest additional measures of precaution, directed more especially against the risk of ignition by electric sparks, which is now recognised as the cause of most instances of so-called spontaneous firing of benzine.

Textile fabrics (especially undyed wool and silk) and many other materials become electrified when rubbed or when moved quickly in benzine, and sparks may result causing explosion. The risk of sparking is greatly increased when the air is exceptionally dry, *e.g.*, in frosty weather; and if the relative humidity of the air falls much below 70 per cent of saturation, moisture should be added, by steaming or otherwise. This can easily be done if steam jets are available.

(The degree of moisture or dryness of the air can be determined readily by means of the hygrometer. There are several forms of this instrument, obtainable at small cost. The one in common use is known as the *wet and dry bulb hygrometer*: instructions as to its use will be given on application to H.M. Inspectors).

Benzine may be rendered less liable to ignition by electric sparks by the addition of small quantities of certain soaps or other chemicals. For example, "antibenzinpyrin" or the oleate soap mentioned in the Committee's Report;† the proportion to be added does not exceed 1 part in 1000 of spirit. The use of soap in benzine appears to have become general except in rinsing, and to have contributed to the immunity from fire.

All vessels (hydro-extractors, washing and rinsing machines, &c.) containing inflammable spirit should have adequate covers, and should as far as practicable be kept closed during use. The covers should, moreover, be balanced, so that if forced open by explosion they will fall back by their own weight, and cut off the air supply from the burning spirit; or in the case of rinsing vessels which cannot be kept closed during use, an iron cover should be suspended from above by a cord passing to a catch at some distance from the vessel, when in emergency it can be im-

mediately set free so that the cover will fall. Attention is also directed to the special safety appliances, such as the Nonex, which are now available for the storage of inflammable spirit.

Used spirit should be conveyed in closed pipes, without exposure to air, to the settlers or still, which should be in a room set apart for the purpose.

Naked lights should not be used in a benzine room. Where incandescent electric light is available, the burners should be in a double air-tight glass cover. Failing electric light, the room should be lit from outside, through an air-tight window.

By such means the risk of fire and explosion can be greatly lessened, but it is still necessary to make provision for minimising these effects. There should be an ample water supply, with hydrants and hose, in order to prevent the extension of flames, but water should not be used in attempts to extinguish burning spirit. For the latter purpose blankets and a supply of sand should be kept in readiness. Steam jets will be useful in the event of fire, as well as for the preventive purpose of humidification when the air is dry.

All persons employed should wear woollen or other non-inflammable outer garments.

As a fire may cut off the ordinary exit by the door, there should be alternative means of escape by an outside staircase, if the room is not on the ground floor. All persons employed should have clear instructions what to do in case of fire.

Ample space and free ventilation, desirable on other grounds, also tend to lessen the risk of accidents.

Apart from the risk of fire and explosion, injury to health may result from breathing the fumes of benzine, &c., and care should be taken to make the exposure to those fumes as brief as possible. Meals should not be taken in rooms in which inflammable spirit is used, and suitable accommodation should be provided elsewhere. It is desirable that women and young persons exposed to the fumes should be periodically examined by the Certifying Surgeon, in order that if their health is found to suffer from their occupation they may discontinue it either permanently or for such a time as he may direct.

H.M. Inspectors of Factories will be glad to advise in further detail if desired.—B. A. WHITELEGGE, Chief Inspector of Factories.

Home Office, October, 1906.

CORRESPONDENCE.

ESTIMATION OF THE HALOGENS IN ORGANIC SUBSTANCES.

To the Editor of the Chemical News

SIR,—With regard to the interesting note by Mr. L. H. Berry, A.I.C., in the CHEMICAL NEWS of October 19th (vol. xciv., p. 188), on the above subject, I adopted this convenient little method for chlorine determinations nearly twenty years ago, the original idea being taken from a journal.

The following modifications of the method were found advantageous:—Three hooks formed of bent platinum wires are fixed to a long wire, the hooks passing over the edge of the small platinum crucible. The weighed substance is then mixed with pure powdered quicklime, placed in the crucible, pressed down, and the latter inverted in the larger crucible, the space being filled in with coarser material. No sodium carbonate was used; a blowpipe is unnecessary provided the flame is large, the crucibles being heated over a large Bunsen burner, applying the heat gently at first. When cool the long wire, which may have been coiled round the outer crucible for convenience, is

* Factory and Workshop Act, 1901.

† To prepare such a soap, dissolve 1 kilo. of caustic potash or caustic soda in 4 kilos. alcohol. To each litre of this solution add $\frac{1}{4}$ litre oleic acid, and heat the mixture. To keep the salt in solution add to every 100 parts of the mixture, either before or after heating, 250 parts carbon tetrachloride, benzol, benzine, or other suitable solvent. Any other soluble oleate may also be employed.

carefully straightened, and thus forms a handle to the small crucible. The whole is placed in a beaker and covered with water, and then the small crucible raised by means of the wire. Without these precautions a cloud of the material is thrown up on separating the crucibles; the wire is also a convenience in holding the small crucible when washing out the product. After acidulating with nitric acid carbon has to be removed by filtration, and the chlorine in the accumulated filtrate and washings is estimated in the ordinary gravimetric way. Mairogallol, the condensed chlorine derivative from pyrogallol, after re-crystallisation from benzene, gave by this method:—50·34 per cent chlorine; calculated, $C_{18}H_7Cl_{11}O_{10}$ = 50·4 per cent chlorine.

It is noteworthy that the error is on the wrong side in the case of chloral hydrate in Mr. Berry's note, the percentage of Cl being too high; perhaps the introduction of sodium carbonate would account for this, as it is difficult to obtain the salt free from chloride.—I am, &c.,

C. S. STANFORD WEBSTER.

Elm Lane, Redland, Bristol,
October 20, 1906.

NOTICES OF BOOKS.

A History of Chemistry. By F. P. ARMITAGE, M.A., F.C.S. London, New York, and Bombay: Longmans, Green, and Co. 1906.

A COMPLETE history of chemistry of moderate size and price will certainly be regarded as a boon by the earnest student, and this book is admirable in many ways, the only matter for regret being the fact that the author saw fit to bring the subject down only to the enunciation of the Periodic Law by Newlands. The emphasis laid upon the most important agents in the development of the science and the avoidance of too great a mass of detail will recommend the book even in the eyes of those who have access to similar but much larger works, and by judiciously compressing the pre-Lavoisierian period the author has given himself room for a fuller account of the work of chemists of later date; in particular, we may mention the vivid picture drawn of the striking personality of Berzelius. Moreover, the stories of some of the discoveries are worded so skilfully that something of the zest and enthusiasm of the original investigator is transmitted to the reader; for example, the account of Wöhler's synthesis of cyanic acid, and the important questions which it brought to light, is very graphic and inspiring.

Second Report of the Wellcome Research Laboratories at the Gordon Memorial College, Khartoum. By ANDREW BALFOUR, M.D., B.Sc., F.R.C.P. (Edin.), D.P.H. (Camb.), Director. Khartoum: Department of Education, Sudan Government. 1906.

THE second report of the Wellcome Research Laboratories is a record of steady progress in the valuable work which is being done by the Director and his staff. The greater part of the book is devoted to the reports of the biological and bacteriological work done in the laboratories, and is beautifully illustrated by valuable and in some cases unique photographs. As regards the chemical department, to the head of which Dr. William Beam has been comparatively recently elected, much work has been done in analysing the waters of the Nile, seeds of various kinds, and milk, while an important series of researches on gums has been begun, which should have a valuable influence upon the development of the Sudanese gum industry. Although most of the work is necessarily of a routine nature it is interesting to notice that some new practical suggestions have emanated from this laboratory; such are the improved form of hydrometer, in which a float facilitates accuracy of

readings, and a simplification of the mode of determining crude fibre with an inverted condenser. The apparatus shown is certainly worth a trial by analysts, especially by those who do much agricultural work, although it might appear that the danger of breakage by bumping would be much increased unless special measures were taken to prevent it.

German Scientific and Technological Reader. Books I. and II. By E. CLASSEN, B.A., and J. LUSTGARTEN, M.Sc. London and New York: Harper and Brothers. 1906.

IT is now generally acknowledged that some knowledge of German, sufficient at any rate to enable him to read the language easily, is absolutely indispensable to the student of science and technology, and these two volumes are designed to provide material for reading, graduated in difficulty. Volume I. begins with easy passages, such as a student who has no previous knowledge of the language should be able to cope with, the subjects being connected with physics, chemistry, and various branches of technology; a vocabulary is provided, but is hardly an acquisition, for in many respects it is not nearly full enough, words which are not used in the usual sense in the text being wanting, while, on the other hand, many which have the same form in English as in German are included; thus, we find Nickel and Mangan given, but Vorlage is not translated. Moreover, the vocabulary is not by any means free from errors; for instance, Knallgas does not mean hydrogen, nor Kalk calcium, and Brennwasser is also incorrectly rendered. The second volume contains extracts of greater difficulty, without vocabulary or notes, and it seems probable that the student who could translate them unaided would probably be able to manage an original paper of ordinary difficulty, or at any rate would be spending his time more profitably in the attempt.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 14, October 1, 1906.

Constituents of Manganese and Molybdenum Alloys.—G. Arrivant.—The author described in a previous paper his method of preparation of a series of manganese and molybdenum alloys containing two definite constituents, Mn_6Mo and Mn_4Mo . He now investigates alloys richer in molybdenum. The fusion of the latter is difficult to effect by means of a Schlössing furnace, but by reducing by means of aluminium powder mixtures of oxides in suitable proportions, an alloy containing 75 per cent of molybdenum can be obtained. The substances thus prepared are generally free from aluminium. The alloys are hard, more so as the proportion of molybdenum is increased; they are not magnetic, and the air has no action upon them, but nitric acid completely dissolves them, forming molybdic acid when heated. The author is able to separate three distinct constituents, corresponding to the simple formulæ Mn_2Mo , $MnMo$, and $MnMo_2$, and on examination finds them to consist of crystalline metallic powders of steel-grey colour, non-magnetic, and produced with contraction; their density at 0° being higher than the theoretic density.

Syntheses in the Quinoleic Group. Dicarboxy-dihydrophenylnaphthoquinoleic Ether and its Derivatives.—L. J. Simon and Ch. Manguin.—The base phenylnaphthoquinone, $C_{19}H_{13}N$, is slightly soluble in

boiling alcohol, and, on cooling, crystallises in white flakes. It is slightly soluble in ether, but its best solvent seems to be acetic acid. Its solutions show blue fluorescence. It melts at 188—189° and distils without decomposition at 360°. The authors isolate and analyse the picrate, chlorohydrate, bichromate, and chloroplatinate, and identifies the base with that prepared by Döbner. The identity of the two bases also leads them directly to conclude the identity of the two acids.

MISCELLANEOUS.

Appointment.—Dr. H. A. D. Jowett, who has been appointed manager of works of Burroughs Wellcome and Co., for nearly ten years acted as chief research chemist under Dr. F. B. Power in the Wellcome Chemical Research Laboratories, and during his connection with these laboratories he conducted a number of important investigations, notably on the chemistry of the jaborandi alkaloids, the constituents of cascara, &c. In October, 1905, he relinquished that post on his appointment as Chief of the Experimental Department at the Dartford Works of Burroughs Wellcome and Co. Dr. Jowett has distinguished himself at every step of his career. A Bell scholar in 1891, he passed the minor and major examinations of the Pharmaceutical Society, and secured the Pereira Medal and Redwood Scholarship in 1892. The year following he graduated as B.Sc. London. Between 1894 and 1896 he acted as Assistant Lecturer in Chemistry to the Pharmaceutical Society and Demonstrator in its Research Laboratories; and in 1896 took his degree of Doctor of Science at the London University. During the present year he has been elected a Member of Council of the Chemical Society.

MEETINGS FOR THE WEEK.

THURSDAY, Nov. 1st.—Chemical, 8.30. "A Development of the Atomic Theory which correlates Chemical and Crystalline Structure and leads to a Demonstration of the Nature of Valency," by W. Barlow and W. J. Pope. "Explosive Combustion of Hydrocarbons" (II) by W. A. Bone, J. Drugman, and G. W. Andrew. "Contributions to the Theory of Solutions"—I., Nature of the Molecular Arrangement in Aqueous Mixtures of the Lower Alcohols and Acids of the Paraffin Series; II., Molecular Complexity in the Liquid State; III., Theory of the Intermiscibility of Liquids," by J. Holmes. "The Hydrolysis of Nitro-cellulose and Nitro-glycerin," by O. Silberrad and R. C. Farmer. "Determination of the Rate of Chemical Change by Measurement of the Gases Evolved," by F. E. E. Lamplough. "Experiments on the Synthesis of the Terpenes—IX, Preparation of δ -Ketoheptahydrobenzoic Acid (δ Ketocyclohexanecarboxylic Acid) and of γ -Ketocyclopentanecarboxylic Acid," by F. W. Kay and W. H. Perkin, jun.; X., "Synthesis of Δ -*m*-Mentheneol (8) and of Carvestrene," by W. H. Perkin, jun., and G. Tattersall. "Some Derivatives of Catechol, Pyrogallol, Benzophenone, and of other Substances allied to the Natural Colouring Matters," by W. H. Perkin, jun., and C. Weizmann.

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THE CAUSE OF THE FOGGING OF PLATES IN TROPICAL CLIMATES.

By JOHN McDOWALL, F.C.S.

SOME time ago, while in Upper Egypt, I had occasion to use a full-plate camera with wooden double dark slides. I found the plates to be nearly always fogged, notwithstanding the fact that the slides were perfectly light-tight and all the ordinary precautions of the dark room were taken.

The fogging sometimes showed itself as an opaque clouding all over the plate; sometimes the outline of the woodwork of the slide could be seen, and sometimes the grain of the wood was distinctly visible.

Shortly after I had made these observations, an eclipse of the sun occurred which was total at Assuan, and many scientific men went there to photograph it. On developing their plates, they found that many of them were rendered worthless or their value as a scientific record was greatly diminished by the same kind of fogging which I have described, and they were at a loss to explain it, although some suggested radio-activity as a cause. I have recently investigated this, and herewith give what appears to be the explanation.

I took a quarter-plate double dark slide and placed two Special Rapid plates in it. On the one plate I put a thin piece of tissue paper, in the centre of which I had cut out a star-shaped hole; on the other plate I put an ordinary glass microscopic slide. These objects were inside the slide, and in actual contact with the film. I then placed the double dark slide in a metal box and heated it up to about 40° C., which is the average temperature of Upper Egypt in the summer time. The slide was placed on a porcelain support in the metal box, which was heated by a lamp.

After heating for fifteen hours I developed the plates, and found them to be very strongly fogged, the film being quite opaque; but under the place where the thin tissue paper was, and also under where the microscopic slide was, there was no fogging. In the centre of the tissue paper I had cut a star-shaped hole, and on the plate opposite this was a star-shaped mark which was quite opaque.

I tried various other objects, and found that they acted in a similar manner.

The fact that the agent which produced the fogging could not penetrate glass or transparent tissue paper shows that it cannot be due to ethereal vibrations at all of the nature of light. It is due to vapours which are occluded in the wood at ordinary temperatures, but which are exhaled when the wood is heated. These vapours, which may be peroxide of hydrogen or volatile organic compounds from the varnish, possess the chemical property of reducing the salts of silver which are contained in the film, so that on development the plate appears to have been exposed to the light.

I tried another experiment by fixing a piece of brass tubing in a hole cut in the slide and making the joint light-tight, a plate was then put in and the whole heated to 40° C. in the metal box as before.

The brass tube was connected to a water-pump, by which the vapours in the immediate vicinity of the tube were aspirated out. The fogging appeared to be less under the place where the tube was than on any other part of the plate.

The value of these experiments to the photographer going abroad is apparent. He should get a thin piece of glass or mica with which to cover the plate in the dark slide and protect it from the vapours, and fogging would be entirely prevented by this means.

If the dark slide was opened and heated for some days, there is little doubt but that the vapour which causes the fogging would be expelled, and it could then be used with confidence in the tropics.

The simplest method of preventing the fogging is to paste a piece of paper over the inside of the wooden sliding pieces which are pulled out when the plate is about to be exposed, which effectually prevents the vapour from diffusing out of the wood on to the photographic plate.

SOME APPLICATIONS OF THE THEORY OF ELECTRIC DISCHARGE TO SPECTROSCOPY.*

By Prof. JOSEPH JOHN THOMSON, M.A., D.Sc., F.R.S., &c.,
Professor of Natural Philosophy, R.I.

(Concluded from p. 199.)

Application of these Results to Spectroscopy.—We have seen that the passage from the dark to the luminous discharge occurs with great abruptness, an increase of the potential difference by $\frac{1}{100}$ th of a volt being sufficient under certain circumstances to convert a discharge in which no luminosity at all could be detected to one where it was quite bright. This suggests that the luminosity sets in when the internal energy of the atom—or rather of that part of it which gives rise to the particular kind of light present in the luminous discharge—attains a perfectly definite value. This way of regarding the origin of the luminosity affords a very simple explanation of the variation of the spectrum with the kind of discharge, and of the effect of introducing capacity or self-induction into the circuit containing the discharge tube. Let us consider the rise in energy of a vibrating system inside the atom. Let E be the energy at the time t ; α the rate at which it is absorbing the work done in the discharge tube. The energy may be supplied to it from the Röntgen radiation in the tube, or from the corpuscles which come into collision with the atom; α will be proportional to the rate at which the electric field producing the discharge is doing work in the neighbourhood of the atom we are considering. It will thus be proportional to the product of the electric force and the flux of corpuscles in this neighbourhood. Let us suppose that the system radiates energy at a rate proportional to E , say, equal to βE ; then we have—

$$\frac{dE}{dt} = \alpha - \beta E,$$

or—

$$E = \frac{\alpha}{\beta} (1 - e^{-\beta t}),$$

if $E = 0$ when $t = 0$.

Consider two different systems A and B in the same atom. Let E_1, α_1, β_1 ; E_2, α_2, β_2 be the values of E, α, β for the systems A and B respectively:—

$$E_1 = \frac{\alpha_1}{\beta_1} (1 - e^{-\beta_1 t}),$$

$$E_2 = \frac{\alpha_2}{\beta_2} (1 - e^{-\beta_2 t}).$$

Now suppose that the system A is one that does not absorb much, but also does not radiate much, while B absorbs a great deal more than A, but radiates still more in proportion, so that $\alpha_2 > \alpha_1$, but $\alpha_1/\beta_1 > \alpha_2/\beta_2$, so that ultimately E_1 is greater than E_2 , but at first E_2 is greater than E_1 . The curves (1) and (2), Fig. 4, represent the variations of E_1 and E_2 with the time.

Suppose now that systems A and B become luminous when the internal energy is equal to W . It is not necessary to assume that the critical amount of energy is the same for the two systems, the assumption is only made to simplify the diagram; the reader will see that the argument

* A Discourse delivered at the Royal Institution, January 19, 1906.

would apply if the critical amounts of energy were different in the two cases.

Now consider first the case when the rate at which work is being done in the tube is so small that though a_1/b_1 is greater than W , a_2/b_2 is less than W , the case represented in Fig. 4; here system A acquires the amount of energy necessary to make it luminous, while system B does not; thus in this case the spectrum of the gas would show the lines corresponding to A but not those of B. Suppose now we increase the rate at which work is done in the tube, so that both a_2/b_2 and a_1/b_1 are greater than W , the case represented in Fig. 5.

Here the system B attains the critical amount of energy, and it reaches this value before A does, so that in this case the lines of B will be visible. Let us now consider the lines in the spectrum corresponding to the system A; these will be visible if the energy in the system reaches the critical value; the conditions in this case are in some respects more unfavourable for the supply of energy to this system than they were in the previous one. For in the first case the system B got into the condition in which it radiated as much energy as it received, and thus did not absorb any of the energy; in the second case, however, B became luminous before its radiation was equal to the absorption; it is thus taking in more energy than it gives out, and this may result in a diminution in the rate of supply of energy to A; it would do so, for example, to a marked extent if the conditions were such that A received

forces do work will be proportional to the electric force. As this is much greater near the cathode than at other parts of the tube, we should expect the lines of systems of the type B to preponderate near the cathode, and to be absent or much feebler in other parts of the tube. If the tube were of the type frequently used for spectroscopic purposes, with a capillary portion in the middle, then, since the current density is much greater in this portion than in any other, the rate of work per unit volume of the gas will be much greater in the capillary portions than in the wide parts of the tube, and we should therefore expect the lines of systems of the type B to be much more prominent in the capillary part than in the wide part.

Effect of Self-induction and Capacity.—Suppose that we have a tube of uniform bore arranged as in Fig. 6, the terminals of the tube being connected with the plates of a condenser of capacity C , and that there is a coil whose coefficient of self-induction is L , placed in series with the tube; then if the discharge through the coil begins when the potential difference between the plates of the condenser is V_0 , the potential difference between the plates after a time t will be—

$$V_0 \cos pt,$$

and the current through the tube—

$$C V_0 p \sin pt,$$

$$\text{where } p = \frac{1}{\sqrt{LC}}.$$

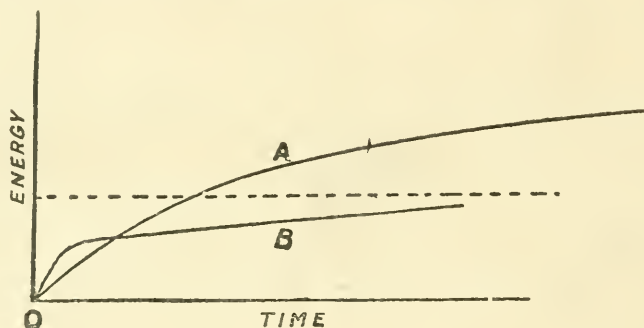


FIG. 4.

a considerable portion of its supply of energy from B. This diminution in the supply might be great enough to prevent the internal energy in B reaching the critical value. Thus the result of the increase in the rate of supply of the electrical energy might be to weaken or even obliterate the lines of A, and while with the smaller rate we had the lines of A and not those of B, with the larger rate we might have the lines of B and not those of A. Thus an increase in the rate at which the electric field is doing work, such as would be produced by increasing the current through the discharge tube, might result in an entire change of the spectrum. We should expect that it would only be in exceptional cases that the lines of A would be obliterated under the conditions holding in case A, but in all cases the increase in the brilliancy of the lines of B would be large compared with the increase of those in A.

We see from the equations giving E_1 and E_2 that until the supply of energy has lasted for a time comparable with $1/b_2$, E_2 is large compared with E_1 ; thus for electrical discharges which last for an exceedingly short time we might easily have the lines of B visible and not those of A.

In a discharge tube conveying an electric current, the amount of work per unit volume of the gas done by the electrical forces per unit time varies very largely from one point of the tube to another. If the cross section of the discharge is the same at all parts of the tube, so that the current density is uniform, the rate at which the electrical

Thus the maximum value of the product of the current and the potential difference, i.e., rate at which the electric forces are doing work in the tube, is—

$$C V_0^2 p, \text{ or } \sqrt{\frac{C}{L}} V_0^2,$$

and is thus proportional to the square root of the capacity, and inversely proportional to the square root of the self-induction. Thus, increasing the capacity increases the maximum rate of work, and therefore increases the brilliancy of the lines corresponding to systems of the type B relatively to those of type A, while inserting self-induction in the circuit increases the brilliancy of those of type A as compared with those of type B. If we suppose that the "blue" spectrum of argon corresponds to a system of type B, the red to a system of type A, we have an explanation of the changes in the spectrum of this gas, for by inserting capacity in the circuit we can change from the red to the blue spectrum, while having got the blue we can get back to the red by inserting self-induction as well as capacity. I have here a little model which is intended to illustrate the way in which the red and blue spectra of argon originate. It is based on the fact that when we send a current of electricity through a circuit, the current does not rise to its steady value instantaneously, but, starting from zero, increases with the time in exactly the same way as we have supposed the intrinsic energy in the atom, i.e.,

the way represented by the curve in Fig. 4. The quantity in the electrical case corresponding to the radiation λ is the resistance of the circuit divided by the self-induction, while the quantity a is inversely proportional to the self-induction. Thus, a circuit with large self-induction and small resistance is analogous to the system A, while one with small self-induction and large resistance is analogous to a system of type B. Now my model of the argon atom consists of two circuits, C and D, placed in parallel. C has large self-induction and small resistance, D has little self-induction but large resistance. An electric lamp is placed in each circuit. If I supply energy in one way, *i.e.*, by continuous current to the system, the red lamp in C lights up and the blue lamp in D is dark, while if fed by an alternating current, the blue lamp shines and the red is dark. It would be interesting to see whether, as we gradually diminish the self-induction, we get the whole of the lines in the blue spectrum at once, or whether the lines of this spectrum enter in groups one after the other. I have tried somewhat similar experiments with the hot lime cathode to see in a mixture of gases (mercury vapour and air) which spectrum first appeared as the rate of doing work in the gas was gradually increased. The great difficulty in this determination is that when once the luminosity begins there is such a rapid increase in the ionisation that the current through the gas and the rate of

the rate at which work is being done at any part of the tube is approximately proportional to the rate at which heat is being produced in the tube. I do not, however, regard temperature, *i.e.*, the energy due to the translation of the atoms as a whole, as having any direct connection with the production of spectra. The work done by the electric field on the corpuscles is, since the corpuscles can easily penetrate the atoms of the gas, first converted into internal atomic energy. This energy may ultimately be for the most part transformed into the energy of translation of the molecules of the gas and so appear as temperature, but it by no means follows that, if we heated the molecules of the gas by non-electrical means to the temperature to which even a few of its molecules are raised by the electric discharge, that we should get a luminous spectrum. The production of the spectrum depends upon the internal energy of the atom. When we use the electric discharge, all the work done by the corpuscles goes at first into the form of internal atomic energy, while if we supplied the same amount of energy to the gas by thermal, as distinguished from electrical means, the energy would go first into increasing the energy of translation of the atoms, and very little of it would ever get inside the atom. It is probable, however, that some of the energy of translation would get converted into internal energy, and that temperature is one way of giving internal energy to the atom

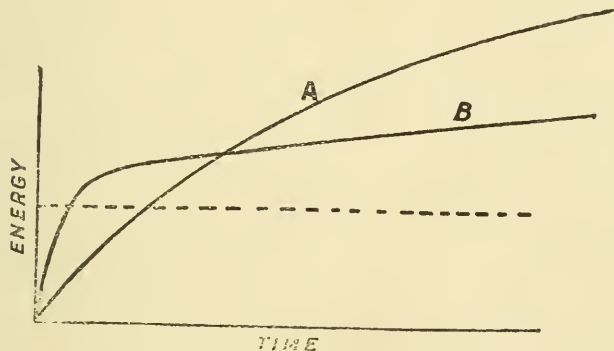


FIG. 5.

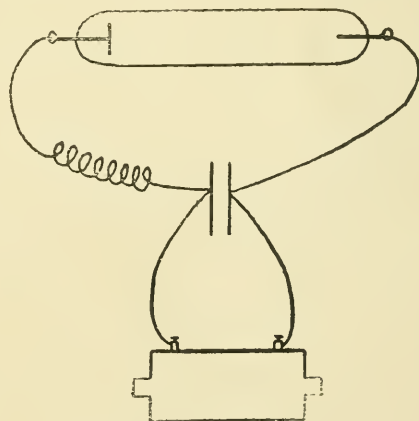


FIG. 6.

doing work increase in an exceedingly short time through a wide range of values, and thus a gradual increase in the rate of work is exceedingly difficult to obtain; on several occasions, however, I was convinced that on gradually increasing the rate of work, the mercury lines were the first to appear, and were the last to disappear, when the rate of work was reduced from a high value, at which both the nitrogen and mercury spectra were bright down to a point where the discharge ceased to be luminous.

The preceding considerations have also an important application to the difference between the arc and spark spectra. In the continuous arc discharge, although the average rate of work is much higher than in the spark, the maximum rate is very much less; in the spark discharge we have exceedingly intense current density lasting for a very short time, and while the spark is passing we have a very much greater rate of work than in the arc. Hence, the state of things in the spark will be analogous to that represented in Fig. 5, and the lines corresponding to systems of the type B will be enhanced relatively to those of type A; we conclude then that the arc lines correspond to systems of the type A, the spark lines to those of type B.

The work done in the discharge tube is probably ultimately converted for the most part into heat, so that

and so producing luminosity. From one point of view, however, it is a very extravagant method, as the fraction of the energy spent in heating the gas which goes in producing luminosity is small.

The coefficient of absorption a of the systems will depend upon the way in which the internal energy is given to the atom, as well as upon the rate at which the electric field is doing work in the neighbourhood of the atom. Thus, for example, if the internal work is given by means of rapidly moving corpuscles, the coefficient of absorption will depend upon the velocity of the corpuscle, for we can easily show that when a corpuscle passes at a fixed distance from a system of corpuscles having a definite period of vibration, there is one velocity of the corpuscle, depending on this period—fast if the period is short, slow if it is long—for which the energy given by the corpuscle to the system is a maximum. Thus the relation between the amounts of energy absorbed by two systems from the corpuscles depends upon the velocity of the corpuscle. The velocity of the corpuscles in a discharge tube depends upon the pressure of the gas, so that even though the rate at which the electrical forces are doing work may be the same at two different pressures, the relative intensities of the lines of two systems A and B may be different.

Again, we might expect that the coefficient of the rate

of absorption of energy would be different according as the energy is given to the atom by means of the large systems which form the positive ions, or by means of small corpuscles; and that the relative brightness of lines might be different in the two cases. In the Canal-Strahlen we have positive ions moving through gas and producing luminosity, and the spectrum of this luminosity possesses interesting peculiarities differentiating it from the spectrum of other parts of the tube. Perhaps the most striking difference, however, is when the positive ions strike against a salt like lithium chloride; they make the red lithium line appear with great brilliancy, while if corpuscles strike against the chloride the red line is not visible. It is remarkable that the spectrum of the metal is produced much more readily by the positive ions when they strike against a salt of the metal than when they strike against the metal itself. This is shown in a striking way; if we take the liquid alloy of sodium and potassium and direct a stream of Canal-Strahlen upon it, the clean parts of the alloy appear quite dark, but the specks of oxide scattered over its surface shine with a bright yellow light, giving the sodium spectrum.

When the internal energy of the atom is increased by means of light, as in Professor Wood's beautiful experiments on the fluorescence of sodium vapour, the coefficient of absorption of a system will depend upon the relations between the periods of that system and the period of the light vibrations incident upon them. Thus, as Professor Wood found to be the case, the numerous lines in the spectrum given out by the vapour alter greatly in character and wave-length when the period of the incident light is changed.

The same principles which explain the variation in the intensities of the spectra given out by two different systems in the same atom, can be applied to explain the variations in the intensities of the spectra of two gases A and B when these are mixed together. We know that under some conditions the lines of only one constituent of the mixture appear, while under others we get the lines of both the gases. Let us suppose that the lines of A appear with a lower rate of work of the electric forces than those of B, and that we send a constant current through the discharge tube. We can calculate what the electric force must be to produce from the molecules of A alone the number of ions required to carry this current; having found the electric force on this supposition, we can, knowing the current, find the rate at which the electric forces would be doing work in the tube. If this rate of work is less than that required to make B luminous, the current will be carried by the ions of A alone, and the spectrum of B will not be developed; if the rate of work on this supposition is greater than that required to make B luminous, the spectrum of B will appear, and it must take a share in carrying the current. Let us suppose that we have so much of A present that the rate of work is not sufficient to develop the spectrum of B, and consider what will happen as the proportion of A is diminished. In order to supply the number of ions required to carry the given current from the smaller number of molecules of A, the electric force, and therefore the rate of work in the tube, must, on the supposition that the current is wholly carried by A, increase, and if we continually diminish the amount of A present, the rate of work will at last reach a value sufficient to make B luminous, with the given current. This stage will give the smallest quantity of A which can, for the given current, wholly swamp the spectrum of B. The rate of work done in the tube will depend on the current going through it, and also on the pressure of the gases, so that both these quantities will influence the proportion of the gas B required to make its spectrum visible.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution will be held on Monday next, November 5th, at 5 p.m.

THE DETERMINATION OF SMALL QUANTITIES OF COPPER IN WATER.*

By EARLE B. PHELPS.

DURING the past few years the question of the addition of small quantities of copper salts to water supplies as a preventative of algal growths and as an emergency disinfectant against typhoid fever germs, has received much discussion and led to many important investigations in this country as well as abroad. One result of all this work has been to indicate the need of some simple yet accurate method for the determination of the small amounts of copper with which the investigator has to deal. The method recommended by the Committee on Standard Methods of Water Analysis of the Laboratory Section of the American Public Health Association ("Report of the Committee on Standard Methods of Water Analysis," *Journ. Inf. Dis.*, 1905, Sup. No. 1, p. 1), is essentially that of Clark and Forbes (Mass. State Board of Health, Third Annual Report for 1900, p. 487). It involves the concentration of a sufficient amount of the water to yield a weighable amount of copper, the precipitation of the copper, as well as of certain other metals which may be present as sulphides, and the separation from the mixed sulphides of the lead and iron by the usual methods. The copper is then deposited electrolytically and weighed. Quantities of copper as small as 2 or 3 m.grms. are thus determined by Clark and Forbes with a mean probable error of about 5 per cent, while the determination of 1 m.grm. obviously cannot be made with a probable error of less than 10 per cent. The disadvantages of the process are, first, the necessity for boiling down a large volume of water in order to get sufficient copper to weigh with accuracy, and, second, the length of time required and the liability of error introduced by the precipitations and separations involved.

Colorimetric methods, while generally much more sensitive than the gravimetric, are greatly influenced by the presence of other substances, especially other metals and organic colouring-matter.

The writer has had occasion to make a number of such copper determinations and was moreover limited by the experimental conditions to quantities of one litre for each determination. Since the water contained at times only a few tenths of a milligram of copper per litre, the standard method of procedure was obviously out of the question. As a result of a study of various possible methods for the determination, a procedure was devised which seemed to combine to a satisfactory degree the requisite sensitiveness, accuracy, and simplicity. The method consists in the evaporation of a given volume of the water to about 100 c.c., the electrolytic separation of the copper from the acidulated solution, the solution of the deposited copper in dilute acid, and its neutralisation and colorimetric determination as sulphide, by comparison with standard tubes of known copper content. By this procedure it is easily possible to determine 0.1 m.grm. of copper, or if this amount were derived from a litre of water, 0.1 part per million. The accuracy is fully as great as with the gravimetric method using ten times as much of the same water.

The detailed procedure is as follows:—

Apparatus.—Platinum dishes of about 100 c.c. capacity to serve as anodes. Connection with the circuit is most conveniently made by placing the dish in a little mercury, contained in a shallow metal dish. To the latter is soldered a wire leading to the positive binding post.

A stout platinum wire, about 50 c.m. long, 40 c.m. of which is coiled into a flat spiral, and whose end is fastened directly to the negative binding post. The spiral constitutes the cathode.

A convenient source of electrical current. The character of the current is not so important in this case as in gravi-

* Published by permission of the Director of the U.S. Geological Survey. From the *Journal of the American Chemical Society* xxviii., No. 3.

Summary of Copper Determinations.

No.	Water.	Parts per million.		Characteristics of the water.	Substances added.	M.grm. of copper.	
		Total solids.	Loss on ignition.			Taken.	Found.
1.					None	0.54	0.52
2.					None	0.27	0.27
3.					None	0.27	0.24
4.					None	0.14	0.12
5.	Boston tap water..	40	15	Soft, coloured, surface	None	0.14	0.12
6.					Fe as FeCl ₃ , 5 m.grms.; Pb as acetate, 40 m.grms. ..	0.54	0.54
7.					Ag as AgNO ₃ , 0.5 m.grm.; Sn as SnCl ₃ , 1.0 m.grm. ..	0.54	0.57
8.	Chattahoochee, Ga.	300	50	Soft; solids are red iron clay ..	None	0.54	0.57
9.	Pecos, N. Mexico .	2000	100	Hardness of 840 parts; turbid .	None	0.54	0.54
10.	Milk, Mont. . . .	750	—	Hardness of 620 parts; clear ..	None	0.54	0.55
11.	Colorado, Texas ..	300	—	Hardness of 128 parts; turbidity of 110	None	0.54	0.52
12.	Boston sewage ..	4000	810	Chlorine abnormal, about 1500.	None	0.54	0.50
13.	Hay infusion.. ..	—	—	Colour about 300.	None	0.54	0.55
14.	Straw-board waste .	7000	4000	High in CaO and organic acids	None	0.54	0.51

metric processes, since only small amounts of copper are dealt with and the deposit need not be washed or dried. In the present experiments the current was supplied by two "gravity cells" in series, yielding a current through the solution of about 0.02 ampère. The current density at the cathode was about $N.D_{100} = 0.3$ ampère.

Nessler jars of the short type holding 100 c.c.

Reagents.—Standard copper solution. About 0.8 grm. of clean copper sulphate crystals are dissolved in water and, after the addition of 1 c.c. concentrated sulphuric acid, the volume is made up to one litre. In 100 c.c. of this solution the copper is determined in the usual way by electrolytic deposition and weighing, and the solution is diluted so that 1 c.c. contains 0.2 milligram copper. This solution is permanent.

Potassium sulphide reagent. An alkaline solution of potassium sulphide made by mixing equal volumes of 10 per cent potassium hydroxide solution and a saturated solution of hydrogen sulphide in water.

Nitric acid one to three and sulphuric acid one to one, both tested for copper.

The Determination.—Of waters carrying from 0.1 to 1.0 part copper one litre is taken. For other concentrations take proportionate amounts. Evaporate to about 75 c.c. and wash into the platinum dish. Add 2 c.c. of the dilute H₂SO₄ for clear and soft waters. For alkaline waters an additional amount is used to offset the alkalinity. For waters carrying much organic matter or clay, 5 c.c. of acid are added to assure the formation of a soluble copper salt. The dish is then placed in position, the cathode suspended in the solution so that it is parallel to and about half an inch from the bottom, and the circuit is closed. Electrolyse for about four hours with occasional stirring, or over night if convenient. Lift out the cathode without previously having opened the circuit, and immerse the spiral in a small amount of the dilute nitric acid, previously heated to boiling. Wash off the wire and evaporate the nitric acid solution to dryness on the water-bath. If silver is suspected to be present, add a few drops of hydrochloric acid before evaporation. Take up in water and wash into the Nessler jar. Make up to the mark and add 10 c.c. of the sulphide reagent. The colour of the copper sulphide develops at once and is fairly permanent, lasting for several hours at least. A similar tube is prepared by adding 10 c.c. of the reagent to a tube of distilled water and then adding standard copper solution in 0.2 c.c. portions until the colours of the two tubes match. If one litre of water were originally taken, each cubic centimetre of standard solution used represents 0.2 part per million of copper.

The method has been carefully tested as to the completeness of the separation and as to the influence of other substances in the water. Particular care has been taken

to separate small amounts of copper from large amounts of organic matter (sewage and industrial wastes), colouring-matter in surface waters, and from salts of iron, lead, silver, and tin. As will be seen from the appended table of results the separation is in all cases satisfactory. Silver and tin appear to be, according to the authorities, the only metals which will separate out under the conditions used. Neither will be commonly met with. The silver may be converted into the chloride as indicated and does not interfere with the determination. The tin is only partially dissolved by the nitric acid and during the evaporation is converted into metastannic acid. In the alkaline solution used in the test the tin in this form does not interfere in the least.

In the accompanying table are given the results obtained in testing this method. In all cases except those in which Boston sewage and straw-board liquor (the waste liquor of a straw-board mill) were used, one litre of water was taken and the necessary solutions added to it. In the two cases mentioned only 100 c.c. were taken.

A METHOD OF DETERMINING HYDROGEN PEROXIDE : AND FERROUS SALTS AND OTHER REDUCING AGENTS.

By W. E. MATHEWSON and J. W. CALVIN.

THE fact that soluble titanium compounds give a deep yellow compound with hydrogen peroxide forms the basis of well known qualitative tests for both substances (Schönn, *Zeit. Anal. Chem.*, ix., 41, 330). Weller's colorimetric method for the estimation of titanium also depends on this reaction (*Zeit. Anal. Chem.*, xxiii., 410; *Ber.*, xv., 2592). The intensely yellow substance formed, usually considered to be titanium trioxide or the acid derived from it, is instantly decomposed by reducing agents, and it would therefore seem that such compounds might be determined by titrating with standard solution of hydrogen peroxide, using a titanium salt as indicator. It was thought by the writers that if standard peroxide could be used in this way the process might be applied very advantageously in certain determinations. The peroxide is very reactive, and is not only capable of acting as a strong oxidising agent with most reducing substances, but can also reduce many of the stronger oxidising agents, and the method might be equally applicable to some reactions of the latter class. In this paper are given the results obtained with ferrous ammonium sulphate and sodium nitrite. These substances were chosen as they are well known reducing agents, and seemed suitable for testing the method.

Ferrous Ammonium Sulphate.—A standard, approximately 0.1 N solution of ferrous ammonium sulphate, containing some excess of ammonium sulphate, was prepared, several portions of different amounts measured from a burette, about 5 c.c. of phosphoric acid added, to render the solution colourless, and sufficient water to make about 50 c.c. About 5 c.c. of a solution of titanium potassium sulphate was then poured in, and the mixture titrated at once against peroxide. The titanium solution was made by fusing the dioxide with about ten times its weight of potassium hydrogen sulphate, dissolving the fused material in cold dilute sulphuric acid, and filtering. The results obtained from these titrations being quite concordant, four portions of crystallised ferrous ammonium sulphate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, were weighed out, dissolved, and titrated in the same way. The weights of the salt taken were 0.1985, 0.4480, 0.3405, and 0.4641 gm. respectively; the number of c.c. of peroxide taken were 5.73, 12.44, 9.86, and 13.16. The amounts of hydrogen peroxide required for 1 gm. of the iron salt were found, therefore, to be 28.86, 27.77, 28.96, and 28.36 c.c. As ammonium sulphate is stated to make the reaction between permanganate and oxalic acid take place more smoothly and much more rapidly, it was thought that possibly the much greater irregularities observed in these results than in those with the standard solution were due to the presence of excess of ammonium sulphate in the latter. Seven portions of the Mohr's salt were again weighed out, about an equal amount of solid ammonium sulphate added, and the remainder of the operation carried out as before, except that the solution of hydrogen peroxide used was somewhat more concentrated, about 0.15 N. The following are the data obtained:—

No.	Salt taken. Gm.	Peroxide required. C.c.	C.c. of peroxide required per gm. of salt
1	0.1902	3.09	16.24
2	0.3420	5.54	16.19
3	0.4918	7.90	16.07
4	0.5374	8.74	16.26
5	0.6258	10.11	16.15
6	1.1133	17.82	16.01
7	1.4645	23.45	16.01

These results indicate that ferrous iron can be accurately estimated with standard hydrogen peroxide if the titre of the latter be fixed with a known amount of the same substance.

Three weighed portions of the salt were titrated against a peroxide solution, and from the mean the normality of the latter was calculated. The normality was also determined by titration against a carefully standardised permanganate solution. As the effect of slight overstepping of the end-point necessary to give the liquid a tinge of colour to make the normality appear too high in the permanganate-peroxide solution, but too low in that of the iron against the peroxide, considerable care was taken to minimise this error. The titrations were made carefully, and the reaction considered complete when the solution showed just a sufficient tinge of colour to be recognised with certainty. The following are the data:—

Titration of Peroxide against Ferrous Ammonium Sulphate.

No.	Salt taken. Gm.	Peroxide required. C.c.	C.c. of peroxide required per gm. of salt.
1	0.6771	11.54	17.04
2	0.5631	9.66	17.15
3	0.9563	16.23	17.02

Normality of H_2O_2 solution = 0.1498.

Titration of Peroxide against Permanganate.

10 c.c. H_2O_2 solution = 13.37 c.c. KMnO_4 solution.
25 c.c. H_2O_2 solution = 33.35 c.c. KMnO_4 solution:
Normality of H_2O_2 solution = 0.1507.

The agreement is satisfactory considering the strengths of the solutions and the quantities used. As the hydrogen peroxide solution had been prepared by diluting the ordinary pharmaceutical preparation, the slightly higher value obtained with the permanganate may have been due to the presence of traces of foreign matter. As C. E. Smith has shown (*CHEMICAL NEWS*, lxxx., 204), commercial hydrogen peroxide sometimes yields too high results when titrated against potassium permanganate because of the presence of organic substances. Small amounts of these would probably be without influence on the results obtained with ferrous sulphate.

The above indicates a simple method for determining the strength of samples of hydrogen peroxide. The solution is diluted with a known amount of water, so that its strength is reduced to about 0.2 N (0.3 per cent.). About 2 grms. of ferrous ammonium sulphate are weighed out, dissolved in a little water, and a few grms. of ammonium sulphate and some phosphoric acid added. Some of the titanium solution is then poured in and the mixture titrated against the peroxide, the latter being added from a burette.

Sodium Nitrite.—In these experiments solutions of sodium nitrite of about 0.5 N or 0.2 N were used. As by the action of the acid present in the indicator there is a slight loss of nitrous acid when it is first added to the solution, a rough preliminary titration was made to determine the approximate amount of hydrogen peroxide required; then, in the subsequent titration, almost this amount was added, the indicator poured in, and the titration finished. The results obtained, while reasonably concordant, have been uniformly slightly too high. This is probably due, to some extent at least, to the fact that the reaction is quite slow near the end-point. Probably reasonably accurate results can be obtained only when the titre of the peroxide is fixed with a known amount of nitrite.

Work is being continued in this laboratory with a view to testing the application of the above method to the estimation of certain organic compounds, readily oxidised by hydrogen peroxide in acid or in alkaline solutions.

Grateful acknowledgment is hereby made to Prof. J. T. Willard, through whose kindness these tests have been made.—*American Chemical Journal*, xxxvi., No. 2.

THE ATOMIC WEIGHT OF NITROGEN.

IN the last report, for 1906, of the International Committee on Atomic Weights, attention is called to recent work on chlorine and nitrogen which indicates that an entire revision of the atomic weights may soon be necessary, because nearly all of them are based on the assumed accuracy of a few, such as those of silver, chlorine, bromine, sodium, &c., some of which have been changed as a result of the use of improved and more accurate methods. In the report, reference also is made to the fact that nearly all the weights are based on the analyses of several oxyhalogen salts. "Their accuracy is assumed, and all the anomalies which appear in determinations based upon other lines of research are commonly ascribed to undiscovered errors. The assumption may be sustained, but it is not yet beyond the reach of criticism." Among the atomic weights which have been re-determined by the more accurate and logical methods is that of nitrogen. The results obtained by independent workers, using different substances and both gravimetric and volumetric methods, necessitate the acceptance of the value 14.01 instead of the value 14.04 as found by the indirect gravimetric methods, and as adopted by the International Committee on Atomic Weights. This work upon the atomic weight of nitrogen has been carried out by Guye (*Bull. Soc. Chim.*, 1905, [3], xxxiii., 44) and his colleagues at Geneva, and by Gray (*Journ. Chem. Soc.*, 1905, lxxxvii., 1601) in Sir William Ramsay's laboratory

and in the Chemical Institute in Bonn. The basis of the present report is a lecture on the subject delivered by Guye last year before the Chemical Society of Paris. The fact is pointed out that, in the methods used by Stas and his predecessors and followers, as shown in Table I., the values are not very concordant, and are generally higher than the values in Table II., which are based upon determinations of the densities of the gases, corrected by physical-chemical methods.

TABLE I.—From Chemical Data.

		Ratio.	Atomic weight.
1843	Marignac		14·043
1865	Stas		14·055
1900	Dean	AgCN : Ag	14·031
1901	Scott		14·010
1894	Thomsen	HCl : NH ₃	14·021
1896	Hardin	Ag : AgNO ₃	14·01
1904	{ Richards and Archibald {	CsNO ₃ : CsO ₃	14·037
		KNO ₃ : K ₂ O ₃	14·040

TABLE II.—From Physical Data.

	Gases compared.	Method of correction.	Atomic weight.
1905	Rayleigh . . N ₂ and O ₂	Limiting densities.	14·009
	N ₂ O „ O ₂	Limiting densities.	13·996
1898	Berthelot . . N ₂ „ O ₂	Limiting densities.	14·007
1897	Leduc N ₂ „ O ₂	Molecular volumes	14·005
1905	Jaquerod and Perrot . . .	Comparison at high temperatures . .	14·008

Guye points out that the methods which have been used in determining the atomic weight of nitrogen gravimetrically introduce a number of uncertain factors, and increase the probable error of the result. Thus, in the case when the value is determined from a study of the ratio Ag : NH₄Cl, he shows that the atomic weight determined can be expressed by the equation $X = Ar - B$; when r is the ratio of the silver and ammonium chloride, A the assumed known atomic weight of silver, and B the sum of the atomic weights of $4H + Cl$. While the value for r can be determined with considerable accuracy, those for A and B involve greater errors, especially as nearly all of the atomic weights are based on that of silver, and an error here would produce a greater error in the atomic weights of the other substances whose weights have been determined by reference to it. Guye concludes that the errors in the atomic weight of nitrogen, as determined by the classical methods of Stas and his predecessors and followers, vary from $\pm 0·013$ to $\pm 0·039$, and that these methods cannot be used to determine the atomic weight of nitrogen with accuracy in the second decimal place.

On the other hand, by the use of modern physical chemical methods, very concordant and accurate determinations can be made. These values are obtained by determining the ratio of the density of nitrogen to that of other gases, the results being then corrected with due regard to the laws of Boyle, Avogadro, &c. The methods used to correct the densities found are :—

- The reduction of the critical constants;
- The method of limiting densities;
- The method of corresponding densities;
- The method of the molecular volumes.

In this manner results are obtained in which the error is only $\pm 0·003$.

The atomic weight of nitrogen as determined by these methods is 14·008, as shown by the following summary of the results :—

Ratio of	N ₂ and O ₂	(six determinations)	..	14·009
„	N ₂ „ CO	(six determinations)	..	14·006
„	N ₂ O „ CO ₂	(two determinations)	..	14·007
„	NO „ O ₂	(two determinations)	..	14·008

General average .. 14·008

While the older gravimetric methods used to determine the atomic weight of nitrogen are not accurate, owing largely to their unfortunate selection, it is possible to choose substances where both the direct weights and volume relations can be determined in the same substance.

Guye has thus been able, using nitrous oxide, to determine the atomic weight of nitrogen by the two methods. A glass tube, containing a spiral of iron wire, connected by platinum loops fused in the ends of the tube, is first exhausted and weighed, then filled with pure dry nitrous oxide and weighed. If a current is then passed through the spiral the gas is decomposed and the nitrogen formed is absorbed in a tube of coconut charcoal which has been carefully exhausted. The weight of the nitrogen can thus be determined, as can that of the oxygen, by the increase of weight of the tube containing the spiral. This, of course, is a very brief outline of the method and gives no idea of the immense difficulties which had to be overcome before it could be used. The average of one series of five determinations was 14·007, while another, of three determinations, gave 14·004.

In the analysis by volume the same apparatus was used to decompose the gas. The vessel, to which a manometer was attached, was filled with nitrous oxide, which, after its pressure had been determined, was decomposed. By observing the change in pressure, keeping the volume constant, the necessary data could be obtained from which to calculate the atomic weight. The mean of four determinations by this method gave 14·015, which, averaged with the analyses by weight, gives a mean of 14·009, as compared with the atomic weight 14·008 by the physical-chemical method.

Analysis by weight of N₂O (five determinations) .. 14·007
Analysis by weight of N₂O (three determinations) . 14·003
Analysis by volume of N₂O (six determinations) .. 14·015

14·009

That this figure, or, in round numbers, 14·01, is more correct than 14·04 is confirmed by the work of Gray, who used nitric oxide, which was obtained free from nitrous oxide and nitrogen. The nitrous oxide was removed by allowing the impure nitric oxide gas to bubble through several vessels containing liquid nitric oxide in which the nitrous oxide was absorbed. The nitrogen was separated by subliming the nitric oxide containing nitrogen at a low pressure and removing the nitrogen, which was not absorbed under these conditions, by the pump. The gas thus obtained was carefully tested for impurities, its density was determined, and the value corrected to reduce it to that which it would have as a perfect gas, and also to obtain the atomic weight of nitrogen by the gravimetric method. The apparatus used by Gray consisted of a vessel which could be exhausted; it contained a porcelain boat resting upon nickel supports; these served as the two poles of a source of electricity which was used to heat the contents of the boat by means of a platinum wire wound around the boat and connected with the nickel wires. Carefully purified nickel, in a finely divided condition, was placed in the boat. The known weight of nitric oxide could be decomposed by contact with the heated nickel, the free nitrogen absorbed in charcoal and weighed, and the oxygen determined by the increase in weight of the bulb and boat.

The results obtained by this method may be summarised in the following table :—

I.	From the density of nitric oxide corrected by two different methods, twelve results	14·006
II.	From the density of nitrogen gas obtained in the gravimetric analysis, two results	14·008
III.	From the gravimetric analysis of nitric oxide, twenty-two results	14·010

General average, giving each result an equal value 14·0085

From an examination of Tables I. and II. it will be seen that the physical-chemical methods give, in general, more concordant and lower results than the chemical methods. Guye suggests that possibly this may be due to an error in the atomic weight of silver, and presents the following arguments in favour of a lower value:—

Re-calculating sixty determinations of the ratio of silver to silver salts, using the figure 14.01 for nitrogen, the average result for silver is 107.885.

While the atomic weights of carbon, nitrogen, and hydrogen have been accurately determined by the physical-chemical methods, those of chlorine, sulphur, and phosphorus have been obtained by the use of only one gas in each case, and the results have not yet been verified. If these weights are used to re-calculate a number of determinations, an average of 107.905 is obtained for silver.

Dixon and Edgar have determined the atomic weight of chlorine by a direct synthesis of hydrochloric acid, from hydrogen and chlorine; they obtain the value 35.463. The use of this weight in the re-calculation of the atomic weight of silver gives the figure 107.88.

From a consideration of all these facts Guye suggests that the difference in the atomic weight of nitrogen, as obtained by the older gravimetric methods and by the physical-chemical methods, may be due to the use of too high an atomic weight for silver, which probably lies between 107.871 and 107.895, and cannot be as high as 107.93, the value adopted by the Committee on Atomic Weights.—*American Chemical Journal*, xxxv., No. 5.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

The following are abstracts of papers received during the vacation, and published or passed for publication in the *Transactions*:—

151. "Some New Derivatives of Dicyclopentadiene." By ALEXANDER RULE.

The author has prepared a nitrosobromide of dicyclopentadiene similar to the nitrosochloride described by Kraemer and Spilker, and also the corresponding derivatives of monocyclopentadiene. Attempts were made to prepare oxime derivatives, but the yields in each case were poor.

By treating the nitrosobromide with alcoholic sodium ethoxide, an ethoxyisonitroso-derivative was obtained, whilst the oxynitroso-derivative itself was prepared by treating the pyridinium compound of the nitrosochloride with moist silver oxide.

In neither case was it possible to obtain a ketone by further reactions, owing to the instability of the substances.

The piperidine base prepared from the nitrosochloride is a well-characterised derivative, and forms a sparingly soluble hydrochloride. On reduction with sodium in alcoholic solution it is partially converted into a diamine base, which forms an easily soluble hydrochloride and a crystalline platinichloride.

152. "Some Derivatives of 2- and 3-Phenanthrol." By HERBERT HENSTOCK.

2-Phenanthryl ethyl ether was nitrated by adding nitric acid to its solution in glacial acetic acid, and the nitro-derivative yielded an amino-compound with tin and hydrochloric acid. When this was treated with nitrous acid, the diazo-compound, $\text{OEt} \cdot \text{C}_{14}\text{H}_8 \cdot \text{N}_2 \cdot \text{SO}_3 \cdot \text{Na} \cdot 6\text{H}_2\text{O}$, was obtained.

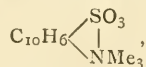
The nitro-compound of the 3-ethyl ether similarly yielded an amino-derivative which can be diazotised.

The 3-nitro-compound, on heating with dry bromine under pressure, gave a 2:7-dibromo-derivative. By oxidation of the 3-ethyl ether with chromium trioxide a phenanthraquinone was obtained which, on treatment with hydroxylamine hydrochloride, yielded a monoxime.

153. "Steric Hindrance in the Naphthalene Series." By CLARENCE SMITH.

Sodium β -naphthylamine-8-sulphonate forms diazoamines with benzene- and *p*-toluene-diazonium chlorides, both being yellow crystalline substances; the former melts and decomposes at 224°, the latter at 219°.

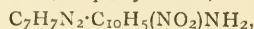
Potassium dimethyl- β -naphthylamine-8-sulphonate, $\text{SO}_3\text{K} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NMe}_2$, obtained from dimethyl sulphate and β -naphthylamine-8-sulphonic acid in alkaline solution, forms colourless crystals easily soluble in water or alcohol. An intermediate product in the preparation, probably anhydrottrimethylaminonaphthalenesulphonic acid,—



is an exceedingly deliquescent, colourless, crystalline substance, soluble in water, insoluble in organic solvents, but has not yet been obtained in the pure state.

The acid, $\text{SO}_3\text{H} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NMe}_2$, forms colourless needles, is sparingly soluble in cold water, dissolves readily in hot water or alcohol, forming solutions with a fine blue fluorescence, and does not react with diazonium salts.

p-Tolylazo-8-nitro- β -naphthylamine,—



forms reddish brown crystals with a green reflex, and melts at 253°.

The influence of steric hindrance is very obvious when the rates are compared at which "G" and "R" salts respectively combine with *p*-toluenediazonium chloride. With approximately one-twentieth molecular solutions, the reaction was complete within five minutes in the latter case, whereas in the former, after fourteen hours, 39 per cent of the diazonium salt, estimated as *p*-tolylazo- β -naphthol, was still uncombined. With a one-fiftieth molecular solution of "G" or "R" salt, after twenty-four hours the amounts of free diazonium salt were 31.0 and 0 per cent respectively.

Sodium 1-bromo- β -naphthol-8-sulphonate,—



obtained from bromine and sodium β -naphthol-8-sulphonate in aqueous solutions, forms colourless glistening leaflets; the halogen is not displaced by diazo-complexes.

154. "Electrolytic Reduction. I. Aromatic Aldehydes." By HERBERT DRAKE LAW.

By the electrolytic reduction of aromatic aldehydes, compounds of the hydrobenzoin type were obtained, the reaction proceeding according to the equation $2\text{X} \cdot \text{CHO} + 2\text{H} = \text{X} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{X}$. Such substituted groups as $-\text{OH}$, $-\text{OCH}_3$, $=\text{O}_2 \cdot \text{CH}_2$, exercise no influence whatever on this reaction; thus vanillin, salicylaldehyde, and piperonal yielded compounds of the above type. Ketones, however, do not show this regularity, the substance formed being contaminated with further reduction products.

155. "Electrolytic Reduction. II. Use of Electrodes." By HERBERT DRAKE LAW.

The velocity of a chemical reaction at the electrodes in an electrolytic experiment is regulated by the rate of diffusion of the solute, and may be represented by the following differential equation:—

$$\frac{dc}{dt} = K(C - C'),$$

C and C' being the concentrations before and after the experiment. Where C' is small, then by substitution of the hydrogen equivalent for C the following equation results:—

$$\frac{I}{Hc} \log \frac{H}{H-h} = K.$$

H represents the hydrogen absorbed at any time, He the total hydrogen required, and h the amount already used. When C' is small, the velocity is almost independent of

the potential of the hydrogen, but otherwise this factor must be taken into account. Further, we have $C - C' \propto 2C' \times P_H$, where P_H is the potential factor (*Analyst*, 1906, xxxi., 3). This, introduced into the above equations, represents the complete action in the absence of catalytic agents.

156. "Studies on Optically Active Carbimides. Part IV. The Resolution of *ac*-Tetrahydro-2-naphthol by means of 1-Menthylcarbimide." By ROBERT HOWSON PICKARD and WILLIAM OSWALD LITTLEBURY.

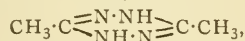
ac-Tetrahydro-2-naphthol has been resolved in a similar manner to α -phenyl- α' -4-hydroxyphenylethane (*Proc.*, xxii., 71).

d-ac-Tetrahydro-2-naphthol 1-menthylcarbamate, separated from the corresponding (*ll*) carbamate by fractional crystallisation from alcohol, melts at 131°, and has $[\alpha]_D -33.4^\circ$ in chloroform.

d-ac-Tetrahydro-2-naphthol is a pale yellow oil, which has $[\alpha]_D +28.2^\circ$ in chloroform and $[\alpha]_D +27.6^\circ$ in benzene. The phenylcarbamate melts at 115–117°, and has $[\alpha]_D +25.2^\circ$ in chloroform.

157. "Tetrazoline." (Part IV.). By SIEGFRIED RUHEMANN.

The author showed that the compounds $C_5H_{11}N_4I$ and $C_5H_{11}N_4I_3$, which C-dimethyltetrazoline,—

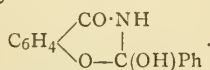


forms with methyl iodide, have properties unlike the corresponding substances $C_3H_7N_4I$ and $C_3H_7N_4I_3$, which are obtained from tetrazoline (Ruhemann and Merriman, *Trans.*, 1905, lxxxviii., 1768). A difference between tetrazoline and C-dimethyltetrazoline has also been observed with regard to the condensation products which these bases yield with aldehydes. The substance which is formed from salicylaldehyde and C-dimethyltetrazoline has the composition $C_{11}H_{12}ON_4 \cdot H_2O$; it therefore contains one molecule of water, which it loses at 100°, and its solution in dilute hydrochloric acid does not give a precipitate with platinic chloride. These properties differ from those of salicylidene tetrazoline and its analogues (*loc. cit.*). On account of these facts the author adheres to the view that the condensation products of aldehydes with tetrazoline are to be represented thus, $R \cdot CH : C \equiv \begin{matrix} N \equiv N \\ NH \cdot N \end{matrix} \equiv CH$.

Bisdiazomethane, $CH_2 \equiv \begin{matrix} N : N \\ N : N \end{matrix} \equiv CH_2$, condenses with only one molecule of an aldehyde to form compounds of the formula $R \cdot CH : C \equiv \begin{matrix} N : N \\ N : N \end{matrix} \equiv CH_2$, which are readily hydrolysed. Their solutions in dilute hydrochloric acid do not yield precipitates with platinic chloride.

158. "Labile Isomerism among Acyl Derivatives of Salicylamide." By JAMES MCCONNAN and ARTHUR WALSH TITHERLEY.

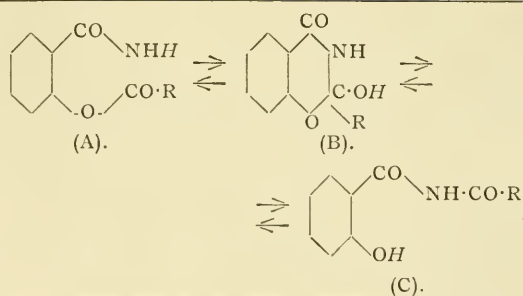
The authors have made a further study of the constitution of Gerhardt's benzoylsalicylamide, which is a tautomeric substance behaving both as *N*-benzoylsalicyl amide and the cyclic metoxazone derivative,—



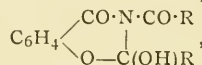
In general, acyl derivatives of salicylamide show remarkable labile characters, and the changes which they undergo may be expressed by the scheme shown in next column.

The possibility of individual existence of *N*-acylsalicylamides apparently depends on the nature of R, and, in general, varying degrees of stability of the types A, B, and C appear, according to the nature of this group, and according to whether the residual hydrogen atom of the NH group is further replaced.

In the case of *O*-acetylsalicylamide (m. p. 138°, which readily re-arranges, the intermediate metoxazone derivative is too unstable to exist, and *N*-acetylsalicylamide (m. p. 147°) results. *O*-Benzoyl-*N*-acetylsalicylamide



(m. p. 96°) passes with extreme ease into *N*-acetyl-2:2-phenylhydroxybenzometoxazone (m. p. 106°), which readily reverts to the open-chain isomeride (m. p. 96°). *O*-Acetyl-*N*-benzoylsalicylamide (m. p. 124°) re-arranges less readily than its isomeride melting at 96°, yielding, however, the same metoxazone derivatives. *N,N*-Diacyl salicylamides, $C_6H_4 \begin{matrix} \diagup CO \cdot N(CO \cdot R)_2 \\ | \\ O - C(OH)R \end{matrix}$, are apparently too unstable to exist, the tendency to re-arrange being so great that the isomeric metoxazone derivative,—



is formed, which in its turn may re-arrange, yielding the open-chain derivative, $C_6H_4 \begin{matrix} \diagup CO \cdot N \cdot CO \cdot R \\ | \\ O - CO \cdot R \end{matrix}$.

159. "The Action of Nitrous Acid on the Arylsulphonylmetadiazines." By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT (with E. G. COUZENS).

The arylsulphonyl derivatives of the ortho- and para-diamines having been shown to yield characteristic diazoimides on treatment with nitrous acid, a series of the arylsulphonylmetadiazines, $R \cdot SO_2 \cdot NH \cdot X \cdot NH_2$, was examined in order to ascertain whether their diazonium chlorides, $R \cdot SO_2 \cdot NH \cdot X \cdot N_2Cl$, would give rise to diazoimides. The monobenzenesulphonyl derivatives of tolylene-2:4-diamine, 4:6-diamino-*m*-xylene, and diaminomesitylene were prepared and subjected to the action of nitrous acid in hydrochloric acid solution; their diazonium chlorides, which were stable in acid solution or in the dry state, underwent decomposition at the ordinary temperature on treatment with sodium acetate, evolving at least 50 per cent, and in some cases even the whole of the diazo-nitrogen, and leaving either arylsulphonylaminophenols or ill-defined azo-derivatives or mixtures of these substances. In no case could any diazoimide be detected.

160. "Dinaphthacridines." By ALFRED SENIER and PERCY CORLETT AUSTIN.

The authors have made a further study of the interaction of methylene di-iodide on naphthylamines, which was introduced by one of them and Goodwin in 1902 as a general method of acridine synthesis. They have also found the requisite conditions for the substitution of methylene dichloride for the di-iodide and of its analogues, ethylidene chloride and benzal chloride, in the synthesis of dinaphthacridines, which renders the preparation of the

α -N- β -CH- β dinaphthacridine much easier.

The notation employed is that proposed by Senier (*Brit. Assoc. Report*, 1903, 616: CHEMICAL NEWS, 1903, lxxxviii., 272).

When methylene dichloride and α -naphthylamine were heated in a closed tube at 230°, α -N- β -CH- β dinaphthacridine was formed. It distils unchanged, melts at 185.5 (189° corr.), not at 173° as previously stated, exhibits triboluminescence, and yields an aurichloride.

α -N- β

Dinaphthacridine, prepared by the methylene

 β -CH- α

dichloride and other new methods, distills unchanged, is not triboluminescent, melts at 223° (228° corr.), and forms a *platinichloride* and *bisdinaphthacridine hexabromide*.

 β -N- β Dinaphthacridine (β -naphthacridine, Reed) was α -CH- α

prepared by the action of methylene dichloride on β -naphthylamine in a closed tube. It is not triboluminescent. Using methylene di-iodide, it was found that, by varying the conditions of the experiment, (1) Reed's base alone, (2) Morgan's base chiefly, or (3) a mixture of the two, could be obtained.

 α -N- α

Methyldinaphthacridine, obtained from ethyl-

 β -CMe- β

idene chloride and α -naphthylamine, forms greenish yellow octahedra melting at 219° (224° corr.), which are not triboluminescent.

The *hydrochloride*, *aurichloride*, *platinichloride*, and *di-bromide* were described.

 α -N- α

Phenyldinaphthacridine, prepared from benzal

 β -CPh- β

chloride and α -naphthylamine in presence of naphthalene, forms yellow hexagonal plates, which are not triboluminescent, and melt at 224° (229° corr.). It yields a *hydrochloride*, *platinichloride*, and *aurichloride*.

 β -N- β

Phenyldinaphthacridine was prepared from

 α -CPh- α

benzal chloride and β -naphthylamine. It is not triboluminescent, and melts at 293° (301.5° corr.).

161. "The Relation of Position Isomerism to Optical Activity. VII. The Rotation of the Menthyl Esters of three Isomeric Dinitrobenzoic Acids." By JULIUS BEREND COHEN and HENRY PERCY ARMES.

The menthyl esters selected for investigation were those of the 2:4-, 2:6-, and 3:5-dinitrobenzoic acids. In a previous communication on this subject (*Trans.*, 1905, lxxxvii., 122) it was shown that of the three mononitroesters the ortho-compound produced the greatest rotation and the para- the least, the meta-ester lying between the two. The present results agree with the former observations. The di-ortho-compound has the highest molecular rotation, $[M]_D - 642^\circ$, and the di-meta- the lowest, $[M]_D - 246^\circ$, whilst the compound which contains one nitro-group in the ortho- and one in the para-position has a constant which is nearly the mean of the other two, namely, $[M]_D - 470^\circ$. At the conclusion of the paper, one of the authors draws attention to the evidences of steric hindrance which are afforded by the action of di-ortho-substituted acid chlorides on menthol.

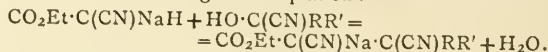
162. "The Properties of 2:3:4:5-Tetrachlorotoluene." (A correction). By JULIUS BEREND COHEN and HENRY DRYSDALE DAKIN.

In a paper on the chlorination of the trichlorotoluenes (*Trans.*, 1904, lxxxv., 1274) it was stated that whereas 3:4:5-trichlorotoluene was converted on chlorination into a tetrachlorotoluene (m. p. 97–98°) which gave a nitro-derivative melting at 159°, 2:3:4:5-tetrachlorotoluene from 2:4:5-trichloronitrotoluene melted at 86–88°, and gave a nitro-derivative having the same melting-point. It is now found that the latter observation is incorrect, and that the tetrachlorotoluene obtained from 2:4:5-trichloronitrotoluene is identical with that prepared by the chlorination of 3:4:5-trichlorotoluene.

163. "A Method for the Formation of Succinic Acid and of its Alkyl Derivatives." By ANNIE HIGSON and JOCELYN FIELD THORPE.

The cyanohydrins of aldehydes and ketones readily react in the cold with the sodium derivative of ethyl cyanoacetate,

forming the sodium derivatives of dicyano-ethyl salts in accordance with the general equation:—



The free ethyl salts can be prepared from these sodium derivatives on treatment with acids, and on hydrolysis may be converted into the corresponding derivatives of succinic acid.

The following cyanohydrins have been investigated:—

- Formaldehydecyanohydrin, giving succinic acid;
- Lactic nitrile, giving methylsuccinic acid;
- Acetonecyanohydrin, giving *asym*-dimethylsuccinic acid;
- Methylethylketonecyanohydrin, giving methylethylsuccinic acid;
- Enantholcyanohydrin, giving hexylsuccinic acid;
- Mandelic nitrile, giving phenylsuccinic acid.

It is further pointed out that the sodium compound which is formed in the condensation may be treated directly with an alkyl iodide, and in this way further alkylated derivatives of succinic acid can be prepared. For example, *cis*- and *trans*-dimethylsuccinic acids were obtained from lactic nitrile and trimethylsuccinic acid from acetonecyanohydrin, in each case by treating the sodium compound formed in the condensation of these cyanohydrins and ethyl sodiocyanoacetate with methyl iodide and hydrolysing the product.

164. "The Gum of *Cochlospermum Gossypium*." By HENRY HALIBURTON ROBINSON.

A small tree, *Cochlospermum Gossypium*, yields a gum which resembles tragacanth in absorbing a large quantity of water, and swelling up to many times its original size; it is also remarkable for its property of slowly giving off acetic acid.

By hydrolysing the gum with dilute sulphuric acid, a dibasic acid of the formula $\text{C}_{23}\text{H}_{36}\text{O}_{21}$ was obtained, for which the name *gondic acid* is proposed. Gondic acid is soluble in water, and is precipitated from its aqueous solution by alcohol as a white amorphous substance; by evaporation it is obtained in colourless transparent flakes. Like gum arabic, it gives a solution having adhesive power. When dried at 100°, 100 parts of the acid neutralise 23.7 parts of barium oxide, and the rotatory power is $[\alpha]_D + 97.7^\circ$; it forms salts by addition and not by replacement; thus, the barium salt is $\text{C}_{23}\text{H}_{36}\text{O}_{21}\cdot\text{BaO}$.

From the liquids from which the gondic acid had been separated, two sugars were obtained; one of these was xylose and the other was a hexose, possibly galactose, although it presented some differences.

The original gum yielded 14 per cent of acetic acid. By prolonged treatment with cold sodium hydroxide solution and then acidifying and dialysing, a clear, viscid, colloid solution was obtained containing a de-acetylated product, which can be precipitated by alcohol in presence of hydrochloric acid. This substance, for which the name *α -cochlospermic acid* is proposed, gelatinises with water, but does not dissolve.

165. "Studies in the Acridine Series. Part IV. The Methylation of Chrysophenol." By ALBERT ERNEST DUNSTAN and JOHN THEODORE HEWITT.

In previous communications, anhydro-bases have been described resulting from the acetylation of 2-amino-3:7-dimethylacridine, benzoflavine, and chrysaniline, conversion into quaternary ammonium compounds, and subsequent removal of the acetyl groups (*Trans.*, 1904, lxxxv., 529; 1905, lxxxvii., 1058; and 1906, lxxxix., 482). Fischer and Körner (*Ber.*, 1884, xvii., 203; *Annalen*, 1886, ccxxvii., 175) examined the chrysophenol which Claus had produced by heating chrysaniline with hydrochloric acid under pressure. The present authors conclude that it is the amino-group in the acridine nucleus which is displaced by hydroxyl, and regard chrysophenol as 2-hydroxy-5-*p*-aminophenylacridine.

This base gave a *diacetyl* derivative which, when treated with dimethyl sulphate, yielded a quaternary ammonium salt. On removal of the acetyl groups, salts of a base were obtained which, when first liberated, is soluble in excess of alkali as well as of acid. This is probably 2-hydroxy-5-p-aminophenyl-10-methylacridanol-5; on drying at 100° it gave an anhydro-base, $C_{20}H_{16}ON_2$. Various derivatives of chrysophenol, the *acetyl* compound, and the base $C_{20}H_{16}ON_2$ were described, and the solutions of the different substances have been examined with regard to fluorescence.

166. "Optically Active reduced Naphthoic Acids. Part III. The Relative Catalytic effect of Bases on the Compounds of Δ^2 -Dihydro-1-naphthoic Acid." By ROBERT HOWSON PICKARD and JOSEPH YATES.

Sodium *d*- Δ^2 -dihydro-1-naphthoate is transformed in aqueous solution in the presence of hydroxyl ions to the salt of the corresponding Δ^1 -acid. The "strengths" of various inorganic and organic bases as regards this specific reagent have been compared and found to correspond roughly with those deduced from the electrical conductivities. The influence of sodium chloride on the velocity of the transformation is very similar to its influence on the velocity of the catalytic hydrolysis of methyl acetate. There is no difference in the rate of transformation of the sodium salts of the dextro- and lævo-acids.

The methyl ester of the *d*- Δ^2 -acid is transformed in the presence of an organic base in an anhydrous organic solvent with a much greater velocity than the transformation of the sodium salt in water.

The methanism of the two transformations is probably different, the ester being transformed in the presence of a tertiary base.

167. "Estimation of Copper by Titanium Trichloride." By EZRA LOBB RHEAD.

Copper may be quickly and accurately estimated by means of a standard solution of titanium trichloride in presence of potassium thiocyanate.

Cupric salts are reduced and the copper precipitated as cuprous thiocyanate in presence of either sulphuric or hydrochloric acid. The end of the reaction may be rendered more distinct by adding a ferrous salt, either mixed with the standard solution or separately. Cupric salts oxidise ferrous salts, and a red colour is produced with the thiocyanate present; its discharge marks the end of the reaction, which is perfectly sharp.

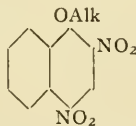
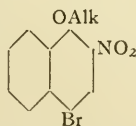
The titration is conducted below 30°, and the whole of the reagent added as quickly as possible.

Ferric and cupric salts may be estimated together, and the amount of iron deducted after being separately determined.

The new method is as accurate as the electrolytic and iodometric methods, and free from the objections and difficulties attaching to them.

168. "Notes on Derivatives of α -N-Alkylated Naphthylamine." By RAPHAEL MELDOLA.

Naphthalene derivatives of the types—



are characterised by the extreme mobility of the alkoxy-group, which is readily exchanged for the alkylamino-group when the compounds in question are treated in alcoholic solution with amines of the type $R \cdot CH_2 \cdot NH_2$. By this means, 2:4-dinitro- α -ethylnaphthylamine (m. p. 169—170°) and 4-bromo-2-nitro- α -benzylnaphthylamine (m. p. 126—127°) and some of their derivatives have been prepared.

The following note has been received during the vacation :—

169. "Note on a Compound of Thiocarbamide and Potassium Iodide." By EMIL ALPHONSE WERNER.

While studying the interaction of iodine and thiocarbamide in aqueous solution, the author incidentally obtained *tetra*-thiocarbamide potassium iodide, $(CSN_2H_4)_4KI$, analogous to the *tetra*-thiocarbamide ammonium bromide, $(CSN_2H_4)_4NH_4Br$, prepared and described by Emerson Reynolds (*Trans.*, 1891, lix., 385). It is formed quantitatively when hot solutions of the separate substances in absolute alcohol are mixed; the new compound crystallises as the liquid cools, in long, delicate, interlacing needles melting at 189—190° and possessing a beautiful satiny lustre, resembling the ammonium bromide compound.

0.3 distilled with an excess of ferric sulphate solution gave 0.08108 iodine; $I = 27.03$. $C_4H_{16}N_8IS_4K$ requires $I = 27.02$ per cent.

The substance is dissociated in dilute aqueous solution, but may be crystallised from a very concentrated solution without sensible decomposition.

All attempts to prepare an analogous, or indeed any compound, from thiocarbamide and sodium iodide were unsuccessful, such a sharp difference in the behaviour of the potassium and sodium salts being rather remarkable.

The compound with ammonium iodide (m. p. 186°) has already been prepared. Potassium bromide and thiocarbamide combine only with difficulty.

NOTICES OF BOOKS.

Modern Soaps, Candles, and Glycerin. By LÉEBERT LLOYD LAMBORN. New York: D. Van Nostrand Company. London: Crosby Lockwood and Son. 1906.

This book will be found more useful to the manufacturer than to the chemist, to supply the former's need of an essentially practical work having been the author's special aim, although a certain amount of theory is necessarily introduced. The mechanical equipment of factories, their general construction and location, are discussed in it, and the problems in engineering which are met with in soap manufacture are treated as fully as space will allow, the subject being regarded almost exclusively from the point of view of the American manufacturer; for instance, in the tables of equivalent prices for soda-ash and for caustic soda, the cost per 100 lbs., &c., is always given in dollars, and most of the illustrations are those of pieces of machinery of American patterns. The most recent improvements in modern methods of making soap and candles and of glycerin recovery are described, and the last mentioned subject is treated very fully, so that for this point alone the book is almost worth its price. The space devoted to chemical analysis, on the other hand, is very restricted, and indeed no more than an outline is given, sufficient only to enable the reader to understand the basis and general method adopted in the examination of the raw materials and factory products, and for the details of the various processes he would probably find it necessary to refer to a treatise on this special branch of analysis.

Church's Laboratory Guide. Revised and partly Rewritten by EDWARD KINCH, F.I.C., &c. Eighth Edition. London: Gurney and Jackson. Edinburgh: Oliver and Boyd. 1906.

MANY improvements have been made in the text of the eighth edition of Church's Laboratory Guide, although the form and general arrangement of the book have not been altered. It maintains its position as an excellent practical book intended more especially for agricultural students, for whom it gives a complete course, beginning with simple chemical operations and qualitative tests, and

passing on to the analysis of manures and feeding stuffs. In the first part of the book the reviser has added some new simple experiments, such as testing manures for nitrogen and the detection of preservatives in milk, to illustrate elementary methods of qualitative analysis and easy chemical manipulations, and new processes have also been added to the section dealing with quantitative analysis, to take the place of the descriptions of those methods which have been superseded since the issue of the seventh edition.

Sechs Vorträge über das Thermodynamische Potential. ("Six Lectures on Thermodynamic Potential"). By J. J. VAN LAAR. Braunschweig: Friedrich Vieweg und Sohn. 1906.

IN these six lectures the author endeavours to show that many of the most complicated problems of chemical equilibrium may be simply and easily solved by applying the theory of thermodynamic potential. Without going very deeply into the mathematical aspects of the subject, he contrives to explain the applicability and value of this important function, and as his language is particularly clear and the thread of his argument easy to follow, even a student who has but little knowledge of physical chemistry should be able to profit by the use of the book. Many quantitative relations regarding the dissociation of gases, solubilities, and melting-points are deduced, and although the treatment is necessarily less full than in larger works, the emphasis laid on important points will recommend the book in the eyes of beginners. The six lectures are preceded by two, on concentrated solutions and on osmotic pressure respectively; in the latter the author argues very convincingly on behalf of the conception of osmotic pressure as the pressure equivalent of an ordinary diffusion process and its non-existence in isolated solutions. The criticisms of the analogy with the gas laws are ably put forward, and the author's contentions are at least worthy of careful consideration by physical chemists.

Untersuchungen über roten Phosphor. ("Researches on Red Phosphorus"). By Dr. A. SIEMENS. Berlin: Julius Springer. 1906.

THESE researches on the properties and behaviour of red phosphorus are of special interest at the present moment when this substance is becoming of rapidly increasing technical importance, and the author's skill in experimental work has enabled him to settle conclusively some disputed points. He has worked out the details of an improved method of detecting small quantities of yellow phosphorus in the red variety, which is more reliable than Mitscherlich's test, and has also carefully investigated the changes effected by rubbing and shaking, proving that these changes consist not in a conversion into the yellow modification, but into a red phosphorus in a more finely divided state. This fresh variety of red phosphorus is more soluble and enters into reactions decidedly more readily than ordinary (red) phosphorus. A complete bibliography of literature relating to Mitscherlich's test and the detection of the element by the reduction of metallic salts, and to the conversion of yellow into red phosphorus, is added.

MEETINGS FOR THE WEEK.

- MONDAY, 5th.—Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "Advantages of Investigating the Unlikely," by Sir William Ramsay, K.C.B., &c.
- WEDNESDAY, 7th.—Society of Public Analysts, 8. "The Analyst and the Medical Man," by Dr. F. Gowland Hopkins.
- FRIDAY, 9th.—Physical, 8. Exhibition and Description of Experiments suitable for Students in a Physics Laboratory, by G. F. C. Searle

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dress, "C. 82," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

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SCIENCE CLASSES, DAY & EVENING—

CHEMISTRY	ALEX. MCKENZIE, Ph.D., D.Sc., M.A.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	V. H. BLACKMAN, M.A.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	J. W. EVANS, D.Sc.
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DIAMONDS.

A Lecture delivered before the British Association at Kimberley.

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Hon. D.Sc. (Oxford, Dublin, and Cape of Good Hope), F.R.S.

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THE CHEMICAL NEWS.

VOL. XCIV., No. 2450.

ON A NEW METHOD FOR THE PREPARATION OF STANDARD SOLUTIONS.

By S. F. ACREE and R. F. BRUNEL.

THE first difficulty that faces the individual beginning a series of exact volumetric analyses in acidimetry and alkalimetry is the preparation of an accurate standard solution of an acid or alkali. Among the acids used for making normal solutions by dissolving weighed amounts in the necessary quantity of water or other solvent, are potassium tetroxalate, oxalic acid, and succinic acid. The chief objection to these is that they are weak acids and cannot be titrated with an error of less than 0.10 per cent. The second objection is that the first two substances cannot be made with a constant amount of water of crystallisation, while if they are prepared in the anhydrous condition they do not long remain so. In solutions made from these substances by students the error may easily be 0.10—0.20 per cent.

Solutions of sulphuric and hydrochloric acids can be standardised fairly accurately by students by the barium sulphate and silver chloride methods, but this involves considerable time and care, and the barium sulphate method, especially, has several objectionable features.

In physical-chemical investigations the writers use standard solutions of hydrochloric acid and alkalis in conductivity water, which must be correct to 0.05 per cent. The standard hydrochloric acid solution is made very quickly and accurately as follows:—A clean litre flask is nearly filled with conductivity water having the room temperature, and is closed with a one-hole rubber stopper through which passes a glass tube drawn out in a long capillary, reaching nearly to the bottom of the vessel.

The flask is weighed to within 0.001 grm., with a similar litre flask filled with water on the other pan. Hydrochloric acid gas, generated from fused pure ammonium chloride and concentrated sulphuric acid and passed through two Wetzel wash-bottles containing sulphuric acid, is run into the flask until the increase in weight is a little more than a grm.-molecular weight. Before the final weighing is taken the solution must be at room temperature. Very little manipulation is required to run the exact amount of hydrochloric acid desired into the flask, but even if considerably more is obtained, the solution can be made up to the required volume by filling the flask up to the litre mark and adding the required extra volume from a burette. The contraction due to mixing 12 c.c. of water with a litre of normal hydrochloric acid solution is only about 0.0001 c.c., or practically nothing. The method adapts itself to the preparation of any smaller volume of solution of any desired strength.

Julius Thomsen (*Zeit. Physik. Chem.*, xiii., 398) tried to determine the atomic weights of hydrogen and oxygen by weighing the quantities of hydrochloric acid gas and ammonia necessary to neutralise each other. His results did not agree with those of other investigators. The reason is now apparent, as several errors were present in his work which could have been excluded.

The first source of error is that due to the absorption of moisture from the atmosphere by the calcium chloride tubes used on the flasks in which the gases were collected and weighed. This error may be quite large, and it is far better not to employ such drying tubes.

The second error is that due to his method of drying the hydrochloric acid gas. Thomsen dried the gas first with concentrated sulphuric acid, the very best method possible, and then *moistened* the gas by passing it over

calcium chloride or magnesium chloride. These chlorides contain considerable water of crystallisation and oxides which would react with the hydrochloric acid and form water. As a result, the hydrochloric acid gas contained some moisture, which made the real amount of hydrogen chloride used smaller than it was thought to be.

The third source of error was in the method of drying the ammonia. Thomsen used potassium and sodium hydroxides in the stick form, in which considerable water is present. Fused potassium hydroxide, afterwards dried well over sulphuric acid, *in vacuo*, would have made this error very small. With these facts in view we shall repeat this work of Thomsen.

The normal solution made in the above way is accurate to within 0.01 per cent. The errors involved in weighing need not be more than 0.002 grm., and the moisture contained in the hydrochloric acid gas is not over 0.00005 grm., judging from the work of Dibbitts (*Zeit. Anal. Chem.*, xv., 121). Such a solution gives no precipitate with barium chloride, is practically free from carbon dioxide, silicates, and all other impurities which are present in the best hydrochloric acid sold in the market. This fact is of the very highest importance to those using such standard solutions for very exact titrations or in physical-chemical investigations involving conductivity measurements. By this method a standard acid solution can be made very quickly, and its error is far smaller than that of the ordinary titration process; it can, therefore, be used directly for titration against alkalis without further standardisation. The solution keeps a long time.

In the same way standard solutions of any dry gases, such as hydrogen bromide, hydrogen iodide, hydrogen sulphide, sulphur dioxide, ammonia, chlorine, &c., in any solvent, can be prepared. The writers use this method for making standard alcoholic hydrochloric acid solutions.

For determining the strength of solutions of pure hydrochloric and sulphuric acids the following plan is much better than the silver chloride and barium sulphate methods. Sodium bicarbonate was crystallised twice and was then free from chlorides, sulphates, and silicates. Approximately 4.12 grms. of this were put into a tall beaker, covered with a watch-glass having a hole in the centre and titrated with the necessary volume, or weight of normal acid—about 50 c.c. For very accurate titrations the carbon dioxide should be removed from the solution in a vacuum, the end-point being obtained when the faintly pink solution remains unchanged in colour after standing in a vacuum for some time. The solution is then evaporated to dryness in a weighed platinum dish and heated to dull redness, until the sodium chloride is dry and the weight constant. A similar platinum dish is treated in the same way and used as a tare. From the weight of the sodium chloride or sodium sulphate and the volume or weight of the acid solution used, the strength of the latter can be easily determined. The total errors of this method should not be more than 0.05 per cent. The titration error should not be over 0.01 c.c. in 50 c.c., or 0.02 per cent, and the weighing error not more than 0.01 per cent. The method can be used for the determination of the strength of a solution of any acid whose sodium salt can be dried and weighed accurately. The titration error is larger with weaker acids.

In a similar manner the exact strength of a solution of pure sodium or potassium hydroxide can be determined by evaporating an exact amount, approximately 50 c.c., with pure hydrochloric acid. The weight of the chloride obtained and the volume or weight of the alkali solution give the data necessary for determining the strength of the alkali solution. The unknown strengths of an acid solution and of an alkali solution can be determined simultaneously by neutralising 50 c.c. of the acid solution with the necessary amount of the alkali solution and evaporating the mixture to dryness, as above. The weight of the dry salt and the volumes of acid and alkali solutions taken furnish the necessary data. The solutions of acid

and alkali must be free from appreciable quantities of silicates, chlorides, sulphates, or other impurities.

Special experiments by Mr. G. H. Shadinger showed that methyl orange is much more sensitive to carbonic acid than is popularly supposed. When carbon dioxide, purified by being passed through two Geissler potash bulbs containing sodium bicarbonate solution, was run into a solution of 3 grms. of sodium chloride in 50 c.c. of water containing a drop of 1:2000 solution of methyl orange, the pink colour produced was discharged by 0.06—0.40 c.c. of 0.1 N potassium hydroxide. Further experiments showed that these solutions, made pink by carbon dioxide, correspond in colour to similar solutions made pink by 0.06—0.20 c.c. of 0.1 N hydrochloric acid, the intensity of the colour varying with the degree of saturation of the solution with the carbon dioxide. When these solutions, saturated with the gas, are vigorously stirred and shaken, as in a titration experiment, the pink colour corresponds to that produced by 0.06—0.10 c.c. 0.1 N hydrochloric acid under the same conditions. Solutions made pink by carbon dioxide become brown very quickly in a vacuum, whereas similar solutions made pink by hydrochloric or sulphuric acid are not changed in colour by such treatment. It is, then, very probable that analyses of carbonates by standard acids in the presence of methyl orange, as ordinarily made, are undertitrated, and the per cent of carbonate found is too low.

Standard Hydrochloric Acid Solutions.

By the method described above, a hydrochloric acid solution was made up to be 0.99987 N. The molecular weight of hydrochloric acid was taken to be 36.458. If the molecular weight 36.471, found by Dixon and Edgar (*CHEM. NEWS*, xci., 263), which is a mean between the values found by Stas and by Richards and Wells (*Journ. Am. Chem. Soc.*, xxvii., 459) were used, the acid would be 0.99953 N.

This solution was analysed by the sodium bicarbonate method described above, but the carbon dioxide was not completely removed from the solutions. This error, however was nearly compensated by the use of the value 23.05 for the atomic weight of sodium instead of 23.01, an error of 0.08 per cent of the weight of sodium chloride. The hydrochloric acid was measured from very carefully calibrated burettes. Three analyses are given in the following table:—

Volume of HCl solution. C.c.	Weight of NaCl. Grms.	Strength of HCl solution.
30.30	1.7730	1.0002 N
30.50	1.7833	0.99937 N
47.24	2.7629	0.99976 N

Average = 0.99972 N, or 0.015 per cent low.

These results show that solutions of hydrochloric acid, prepared as above, are as accurate as any ordinary analytical work requires. The writers believe that the sources of error noted above could be further reduced so that the method would serve for determining the ratio of the atomic weights of chlorine and sodium. For a number of years the value 23.05, obtained by Stas, has been generally accepted, but the recent very accurate work of Richards and Wells gives the value 23.01. If the total errors in the above method can be reduced to 0.02 per cent the writers believe it will furnish reliable evidence in favour of one or the other of the above values for sodium.

A further example of the accuracy and convenience of the sodium bicarbonate method for estimating the strength of acid solutions is given. A normal solution of sulphuric acid was made volumetrically through two other solutions, using about 15 c.c. in the titrations. The titration error might then be about 0.20 per cent. This solution was analysed by the barium sulphate method, the error being not more than 0.10 per cent; 20.68 c.c. gave 2.4170 grms. BaSO₄, or the solution was 1.0013 N. It was then analysed by the sodium bicarbonate method, under the conditions given above, with the following results:—

Volume of H ₂ SO ₄ solution. C.c.	Weight of Na ₂ SO ₄ . Grms.	Strength of H ₂ SO ₄ solution.
47.32	3.3722	1.0026 N
45.33	3.2290	1.0022 N
		Mean = 1.0024

If this last value be considered accurate, the results found by the different methods check very satisfactorily. From the titrations the acid appeared to be exactly normal, but there was a possibility of 0.20 per cent error. The barium sulphate method, with a possible source of error of 0.10 per cent, gave a result 0.11 per cent below that obtained by the bicarbonate method.

Standard Ammonium Hydroxide Solutions.

An attempt was made to prepare standard ammonium hydroxide solutions by passing the dried gas into water in a weighed flask, under conditions similar to those employed in the preparation of standard hydrochloric acid. The concentrated commercial ammonia solution was treated with lime water to remove the carbonates; it was then warmed gently in a flask and the gas was dried by passing it through towers containing quicklime and potassium hydroxide in sticks, and finally through a glass tube six feet in length, filled with broken potassium hydroxide, which had been fused and dried over concentrated sulphuric acid. The gas was then practically free from carbon dioxide and moisture (Van der Plaats, *Rec. Trav. Chim.*, vi., 45), and probably contained very little pyridine.

Several attempts to prepare solutions about 0.2—0.5 N showed that such solutions lose ammonia very quickly when exposed to the air or when transferred to other vessels. That the method could be relied upon to give standard solutions was proved conclusively; such solutions, however, will not remain long unchanged.

A solution was made by passing 1.2450 grms. of ammonia into 250 c.c. of water (N=14.04, H=1.008). This solution was then 0.20184 N. It was analysed as follows:—Normal hydrochloric acid solution, nearly sufficient to neutralise 50 c.c. of the above ammonium hydroxide solution, was run into a beaker. The ammonium hydroxide solution was removed from the flask by means of a 50 c.c. pipette containing a small layer of ligroin to prevent the escape of ammonia, and the solution was immediately allowed to run into the hydrochloric acid solution, the point of the pipette being immersed.

Two analyses showed 50 c.c. of the ammonium hydroxide solution to be equivalent to 14.58 and 14.58 c.c. of normal hydrochloric acid; calculated, 14.59 c.c. The strength of the ammonium hydroxide was 0.2016, or the error in the method was 0.07 per cent.

These standard solutions of hydrochloric acid and ammonium hydroxide are sufficiently accurate to warrant us in believing that the principle of using weighed quantities of well-dried gases for making up standard solutions is one worthy of further study, and this will be done in the near future.—*American Chemical Journal*, xxxvi., No. 2.

Institute of Chemistry.—Examinations in Chemical Technology.—The first examinations in Chemical Technology were held at the Institute from October 16th to 18th, 1906. The examinations were open only to Fellows, and to those Associates who had been registered as such for at least one year. Each candidate was required to produce evidence of practical technological training, and to select one important industry, by which his knowledge of the subjects of the examination might be tested. The candidates who presented themselves on this occasion selected respectively Gas Manufacture, the Oils and Fats Industry, and Steel Manufacture. The papers given on the first day of the examination referred to these industries.

THE ANALYSIS OF DITHIONIC ACID AND THE DITHIONATES.

By R. HARMAN ASHLEY.

ACCORDING to the method of analysis employed by Dymond and Hughes in the examination of potassium dithionate (*Journ. Chem. Soc.*, lxxi., 314), obtained by these investigators as a product of the interaction of potassium permanganate and sulphur dioxide, a weighed amount of the dithionate is dissolved in water, the solution is introduced into a partially vacuous closed flask containing hydrochloric acid, and, after heating, iodine is run in to determine the sulphur dioxide. In this action of hydrochloric acid decomposition takes place according to the equations $\text{BaS}_2\text{O}_6 + 2\text{HCl} = \text{H}_2\text{S}_2\text{O}_6 + \text{BaCl}_2$ and $\text{H}_2\text{S}_2\text{O}_6 = \text{H}_2\text{SO}_4 + \text{SO}_2$. The sulphur dioxide formed is calculated in accordance with the expression $\text{SO}_2 + \text{I}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HI}$. It is to be noted, however, that the procedure of Dymond and Hughes according to which iodine is introduced into the solution of sulphur dioxide was long ago criticised by Finkener (Finkener-Rose, "Quant. Anal.", vi. Auf., p. 837), and for it has been substituted the method suggested by Finkener and elaborated by Volhard (*Ann. Chem. Pharm.*, ccxlii., 94), according to which the solution of sulphur dioxide or the sulphite is introduced slowly from a burette into the iodine solution, the purpose being to obviate the establishment of a secondary reaction, $\text{SO}_2 + 4\text{HI} = 2\text{HO}_2 + \text{S} + 2\text{I}_2$.

It seemed desirable, therefore, to study the decomposition of dithionates by boiling with hydrochloric acid under conditions which would permit the estimation of the evolved sulphur dioxide by bringing it into action in small amounts upon an excess of iodine, in accordance with the principle of the Finkener-Volhard process.

Barium dithionate was chosen as a suitable salt for investigation. It was prepared in the following manner:—Manganese dioxide suspended in water was treated with sulphur dioxide gas in a vessel surrounded with melting ice. After this treatment the solution was made alkaline with an excess of barium hydroxide to remove sulphates and sulphites as well as to convert the manganese dithionate to barium dithionate. The excess of barium hydroxide was removed by introducing carbon dioxide and boiling to break up any acid barium carbonate which might have been formed, and the solution was filtered. The filtrate from the barium carbonate contained pure barium dithionate, which was obtained in solid form by evaporating this solution.

The salt so prepared gave all the reactions of dithionic acid and had a composition corresponding to the formula $\text{BaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$. In determining the composition of the salt two methods were used. In the first, the barium was precipitated by sulphuric acid and weighed as barium sulphate; in the second method the salt was introduced into a platinum crucible and blasted to drive off water and sulphur dioxide, the residue being weighed as barium sulphate.

A salt of the formula $\text{BaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ is said to be formed by slow evaporation ("Watt's Dict.", vol. iv., p. 696). According to my experience, however, the salt crystallised by evaporation over a flame, and that by evaporation at the ordinary temperature in a vacuum over concentrated sulphuric acid had the same composition, and both preparations gave on analysis figures corresponding to the formula $\text{BaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, the results coming within 0.3 per cent of theory. Crystals of barium dithionate are supposed to effloresce, but no evidence of such action was found in my preparations when the crystals were kept in a weighing bottle at ordinary room temperature.

In studying the decomposition of barium dithionate under the action of hydrochloric acid, crystals of the salt were weighed out and transferred into a Voit flask provided with a separating funnel sealed on. The outlet was con-

nected to a Drexel receiver containing a known amount of standardised iodine, and the outlet of this receiver was provided with a trap containing a solution of potassium iodide. Water was first run into the Voit flask through the separating funnel, and the salt was dissolved by the aid of heat. Acid was next run in through the separating funnel and the whole was boiled, a current of carbon dioxide being employed to sweep the sulphur dioxide into the iodine. Hydrochloric acid was added from time to time through the separating funnel to keep up the volume of the liquid and the concentration of the acid. After the operation had proceeded for the times noted, the whole was disconnected and the iodine remaining was determined by means of sodium thiosulphate with starch as an indicator. Results of experiments conducted in this manner are given in Table I.

The irregularity of these results may conceivably be due to one or more of three different reasons. In the first place, it may be that the decomposition of the dithionic acid is not complete, and that this may be so is shown by the fact that after the liquid in Experiment 10 was boiled for an hour and three-quarters and filtered from the precipitated barium sulphate, the addition of sulphuric acid caused further precipitation of barium sulphate. Secondly, it may be that some of the sulphur dioxide escapes absorption in the receiver, if the current of carbon dioxide is passed through the system too rapidly. Thirdly, the concentration of the hydrochloric acid in the receiver tends, as is well known, to render the titration of the residual iodine by sodium thiosulphate less exact and the starch iodide less delicate as an indicator.

To eliminate the concentration of acid in the receiver, in the following experiments sulphuric acid was substituted for hydrochloric acid in the Voit flask. A weighed amount of barium dithionate was introduced into the Voit flask and there dissolved in water. Sulphuric acid was run in through the separating funnel and the mixture then boiled, the sulphur dioxide being collected in the Drexel receiver, trapped as before with potassium iodide. A slow current of carbon dioxide was driven through the system, to sweep the sulphur dioxide into the iodine and to prevent any sucking back. When boiling had been carried so far that fumes of sulphuric acid began to appear, the operation was stopped, and the excess of iodine remaining was determined by means of sodium thiosulphate, starch iodide being used as an indicator. Results of experiments carried out in this manner are given in Table II.

These results show that dithionic acid may be determined by boiling with sulphuric acid and estimating the sulphur dioxide liberated, while when hydrochloric acid is used the results are far from satisfactory.

There are three reasons why sulphuric acid should work better than hydrochloric acid in this process:—

First, when sulphuric acid is added to the solution of barium dithionate, barium sulphate is precipitated and dithionic acid is left in free condition: this reaction proceeding at once to completion, because the barium sulphate formed is removed from the system. It would seem that when hydrochloric acid is used the dithionic acid is completely liberated only by a gradual change in the conditions of equilibrium.

Second, when the solution containing sulphuric acid is boiled, the water is driven off, the concentration of the solution increases, and the high temperature of the fuming-point of sulphuric acid is reached. Under such conditions the decomposition of the dithionic acid is rapid and complete, the time being dependent upon the original dilution of the solution. In one case, No. 11, the operation was ended in four minutes.

Third, no appreciable amount of acid distils over from the Voit flask into the receiver containing the iodine to interfere with the back titration with sodium thiosulphate, the only acid present being that produced by the oxidation of the sulphur dioxide. Under these conditions the starch indicator acts sharply, which is not the case when hydro-

TABLE I.—Decomposition of Barium Dithionate by Boiling with Hydrochloric Acid.

No.	S ₂ O ₅ taken.	I value of S ₂ O ₅ taken.	I taken.	I value of Na ₂ S ₂ O ₃ required.	S ₂ O ₅ found.	Errors in I.	Errors in S ₂ O ₅ .	Time. Minutes.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	
1.	0.0854	0.1898	0.5721	0.3782	0.0872	+0.0041	+0.0018	90
2.	0.1298	0.2885	0.5846	0.2920	0.1316	+0.0041	+0.0018	90
3.	0.1429	0.3177	0.5778	0.2607	0.1426	-0.0006	-0.0003	45
4.	0.1042	0.2317	0.5765	0.3468	0.1033	-0.0020	-0.0009	60
5.	0.1031	0.2293	0.5884	0.3557	0.1047	+0.0034	+0.0016	60
6.	0.0704	0.1564	0.5751	0.4228	0.0685	-0.0041	-0.0019	60
7.	0.0778	0.1729	0.6194	0.4637	0.0700	-0.0172	-0.0078	60
8.	0.1043	0.2319	0.5726	0.3395	0.1048	+0.0012	+0.0005	30
9.	0.1043	0.2319	0.5892	0.3548	0.1054	+0.0025	+0.0011	60
10.	0.1042	0.2317	0.6110	0.3849	0.1017	-0.0056	-0.0025	105

TABLE II.—Decomposition of Barium Dithionate by Boiling with Sulphuric Acid.

1.	0.1039	0.2310	0.5759	0.3435	0.1045	+0.0014	+0.0006	20
2.	0.1046	0.2326	0.5708	0.3372	0.1051	+0.0010	+0.0005	28
3.	0.1039	0.2311	0.5740	0.3435	0.1037	-0.0006	-0.0002	34
4.	0.1033	0.2297	0.5701	0.3387	0.1041	+0.0017	+0.0008	45
5.	0.1721	0.3827	0.5712	0.1876	0.1726	+0.0009	+0.0005	35
6.	0.1719	0.3820	0.5702	0.1894	0.1713	-0.0012	-0.0006	50
7.	0.1726	0.3838	0.5734	0.1898	0.1726	-0.0002	0.0000	12
8.	0.1724	0.3832	0.5727	0.1885	0.1728	+0.0010	+0.0004	10
9.	0.1721	0.3826	0.5727	0.1886	0.1728	+0.0015	+0.0007	10
10.	0.0692	0.1539	0.3130	0.1599	0.0689	-0.0008	-0.0003	12
11.	0.0350	0.0777	0.3109	0.2323	0.0354	+0.0009	+0.0004	4
12.	0.2061	0.4582	0.6205	0.1632	0.2057	-0.0009	-0.0004	15
13.	0.2402	0.5340	0.6215	0.0862	0.2408	+0.0013	+0.0006	15

chloric is used.—*American Journal of Science*, 1906, xxii., p. 259.

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.*

By GREGORY PAUL BAXTER, MURRAY ARNOLD HINES,
and HARRY LOUIS FREVERT.

FROM a recent investigation of the atomic weight of cadmium (Baxter and Hines, *Journ. Am. Chem. Soc.*, 1905, xxvii., 222) the value 112.469 ($A_g = 107.930$) for this constant was obtained by analysis of cadmium chloride. Since this value is nearly one-tenth of a unit higher than the results of recent prior determinations by other investigators, in order to confirm or disprove the higher value the analysis of cadmium bromide was undertaken.

Purification of Materials.

In the previous investigation the cadmium material was purified by fractionally precipitating cadmium sulphide with hydrogen sulphide from an acid solution of cadmium chloride. Two small fractions were rejected, and the next three (which included very nearly all the remainder of the cadmium) were preserved separately. Each one of these three fractions was first thoroughly washed, then dissolved in hydrochloric acid and re-precipitated. Next the precipitates were again dissolved in nitric acid, the nitric acid was expelled by heating with an excess of sulphuric acid, and the sulphate was re-crystallised thrice from pure water. Fraction I. and a portion of Fraction II. were converted into chloride and were analysed in the earlier work, while Fraction III. and a second portion of Fraction II. were converted into bromide.

The method employed for this purpose was that of depositing metallic cadmium electrolytically, dissolving the metal in bromine under water in a quartz dish, and re-crystallising the bromide in platinum vessels. In the first experiments electrolysis was carried on in a solution of the sulphate in pure water between two electrodes of platinum-foil. A sponge of extremely small crystals was thus pro-

duced. These crystals contained occluded sulphate in considerable quantities, and no amount of washing with water was sufficient completely to leach out this occluded material. Hence the bromide made from this metal was sufficiently contaminated with sulphate, which was finally eliminated with difficulty by repeated crystallisation. This bromide was used only in preliminary experiments. More satisfactory results were obtained by depositing the metal upon a platinum dish which had been covered with a very thin film of soft paraffin, so that the deposit could be readily separated from the dish (Richards, *Proc. Amer. Acad.*, 1890, xxv., 200). The cadmium was first washed with water, then with ether, next with alcohol, and finally with water again. This treatment effectually cleansed the metal from paraffin. In order to convert the cadmium into bromide, it was covered in a quartz dish with water slightly acidified with hydrobromic acid, to prevent the formation of basic cadmium salts, and the purest bromine was added in small quantities until the metal was almost wholly dissolved. The solution was heated with the residual metallic cadmium upon a steam-bath until every trace of bromine had disappeared. Then it was filtered with a platinum funnel into a platinum dish, and was re-crystallised three times, with centrifugal drainage in the platinum funnel after each crystallisation (Richards, *Journ. Am. Chem. Soc.*, 1905, xxvii., 110). The original solution contained only traces of sulphate, and, when tested with barium hydroxide, the mother-liquors of the third crystallisation gave absolutely no test for sulphate, hence the crystals themselves must have been pure (Samples II.a and III.a). From the mother-liquors of each fraction, by three crystallisations, similar samples were obtained (Samples II.b and III.b). The crystals were dried over potassium hydroxide in a vacuum desiccator.

Commercial bromine was freed from chlorine by two distillations from a concentrated solution of a bromide, the bromide in the second distillation being almost free from chloride. The bromine was covered with water, and hydrogen sulphide (which had been thoroughly washed with water) was passed into the solution until reduction of the bromine was complete. The solution was boiled, after mechanical separation of the greater part of the free sulphur and bromide of sulphur, and was filtered. Iodine was eliminated by boiling the hydrobromic acid with

* From the *Journal of the American Chemical Society*, xxviii., No. 6.

several small portions of potassium permanganate and rejecting the bromine set free. By heating the remainder of the hydrobromic acid with an excess of permanganate, over half of the bromine was obtained in the free state. The process of reduction with hydrogen sulphide and oxidation with permanganate was then repeated with the resulting bromine, and the final product was re-distilled shortly before use.

One sample of silver was purified especially for this research. The processes to which it was subjected were essentially those which have been repeatedly used in the Harvard Laboratory for the purification of silver. The commercial metal was dissolved in nitric acid, and the solution was filtered and precipitated at considerable dilution with hydrochloric acid. After thorough washing, the precipitate was reduced with invert sugar and sodium hydroxide, and the metallic silver was fused with a blow-pipe on a crucible of the purest lime. In order to cleanse the buttons from surface impurities, they were first scrubbed with moist sand, and then the surface was removed with dilute nitric acid. Next the buttons were dissolved in nitric acid and the solution was reduced with ammonium formate (Richards, Publications of the Carnegie Institution, 1905, No. 28, p. 19; *Journ. Am. Chem. Soc.*, xxvii., 473). The precipitated silver was thoroughly washed, and again fused in a lime crucible. The final process of purification consisted in electrolysis of the silver with a solution of silver nitrate (made from a portion of the silver acting as electrolyte, while the anode was a pile of the pure silver buttons and the cathode a bar of the purest silver). The electrolytic crystals were washed, dried, and fused in a current of pure hydrogen on a lime boat. The buttons were cleansed with dilute nitric acid, and, after drying at 200°, they were cut into fragments with a clean chisel and anvil. Then they were again treated with fresh portions of dilute nitric acid until free from iron, washed, dried, and finally heated to about 400° in a vacuum. This silver was employed in Analyses 4 to 8.

In the first three analyses a mixture of two specimens of silver was employed, both of which had already been used in an investigation upon the atomic weight of iodine by one of us (Baxter, *Proc. Am. Acad.*, 1905, xli., 73). One was prepared from silver nitrate which had been seven times re-crystallised from nitric acid, five times re-crystallised from water, and finally precipitated with ammonium formate. The other was precipitated once as silver chloride, electrolysed once, and finally reduced with ammonium formate.

Water was purified by double distillation with tin condensers, first with alkaline permanganate, finally with a trace of sulphuric acid. Nitric acid was twice distilled with a platinum condenser, the first third of the distillate being rejected in both distillations. The product of the first distillation contained only the merest trace of chlorine.

Method of Analysis.

The method of analysis was essentially that already frequently employed in this laboratory for the analysis of metallic halides. Weighed portions of the bromide, after fusion in nitrogen and hydrobromic acid gases, were first titrated against weighed portions of silver. Then the precipitated silver bromide was collected and weighed.

The apparatus used for the fusion of the salt in hydrobromic acid gas was employed in the preparation of ferrous bromide by one of us (Baxter, *Proc. Am. Acad.*, xxxix., 246), and is a modification of apparatus used for a similar purpose in the determination of the atomic weights of cobalt (Richards and Baxter, *Ibid.*, xxxiii., 117), nickel (Richards and Cushman, *Ibid.*, xxxiii., 99), and uranium (Richards and Merigold, *Ibid.*, xxxvii., 378) in this laboratory. A mixture of air and ammonia was passed over heated rolls of copper gauze, and the excess of ammonia was removed by means of sulphuric acid. The gas was then conducted into an apparatus constructed wholly of glass, with ground joints, which consisted of a tower filled with beads moistened with silver nitrate solution to remove sulphur compounds, two similar towers containing dilute

sulphuric acid to eliminate last traces of ammonia, and two towers filled with sticks of fused potassium hydroxide to absorb moisture and carbon dioxide. The partially dried gas, after bubbling through bromine in a small flask, passed into a second flask containing concentrated hydrobromic acid solution in which washed red phosphorus was suspended, to convert the bromine into hydrobromic acid. A U-tube, also containing red phosphorus and hydrobromic acid, removed traces of bromine which escaped reduction in the flask. Two additional U-tubes containing beads moistened with concentrated hydrobromic acid only, served to eliminate phosphorus compounds which were found, in the investigation upon ferrous bromide (*loc. cit.*), to accompany the hydrobromic acid if the phosphorous acid in the reduction flask was allowed to become very concentrated. Finally, the mixture of nitrogen and hydrobromic acid gases was thoroughly dried, first by pure fused calcium bromide, and then by re-sublimed phosphorus pentoxide.

The cadmium bromide, contained in a weighed platinum boat, was heated gently in a current of nitrogen until a small quantity of residual crystal water was expelled, then strongly in a current of nitrogen and hydrobromic acid until fused. After the salt had cooled, the hydrobromic acid was displaced by nitrogen and this in turn by dry air. The boat was then transferred to the weighing-bottle in which it was originally weighed, and the stopper was inserted without an instant's exposure of the salt to moisture, by means of the bottling apparatus which has been frequently described in papers from this laboratory (Richards and Parker, *Proc. Am. Acad.*, xxxii., lix.). The weighing-bottle was then allowed to stand in a desiccator near the balance case for some time before it was weighed.

Next the boat was transferred to a flask, and the salt was dissolved in about 300 c.c. of the purest water. The weighing-bottle was rinsed, and the rinsings were added to the solution. Then the solution was filtered into the glass-stoppered precipitating flask through a tiny filter to collect a trace of insoluble matter, and the filter-paper and residue were ignited at a low temperature in a weighed porcelain crucible. This residue, which usually amounted to less than 0.1 m.grm. and was never as much as 0.2 m.grm., did not contain detectable quantities of cadmium, and probably consisted of silica and a trace of platinum removed from the boat during the fusion, for the boat, when re-weighed, in most cases was found to have lost a few hundredths of a milligram. No change in weight could be found when the boat was first dried and weighed, then ignited and re-weighed. The difference between the weight of the residue and the loss in weight of the boat was subtracted from the weight of the cadmium bromide.

(To be continued).

Mechanism of Ionisation by Solution.—Gustave D. Hinrichs.—During the solution of a salt in water the contact of the molecules of the solid with the rotating molecules of water electrically insulated produces static electricity. The two electricities, positive and negative, are produced in exactly equal quantities. This electricity cannot escape across the insulated water, and the two atoms of the molecule of the salt are charged. Taking, for example, sodium chloride, the sodium atom receives a positive charge, that of chlorine a negative one. By this means the chemical combination of the two atoms is dissociated, and the two atoms each charged become the ions. If the solution is dilute enough, each molecule of the salt is surrounded by a large number of the non-conducting water molecules. In such a case the ions produced will be well insulated, and can move freely without losing their electric charge. If, however, the solution is stronger, the number of molecules of water for each molecule of salt is diminished, and the molecular insulation of the ions also diminishes; that is to say, the percentage of the molecules in the solution which become ionised diminishes rapidly with the concentration of the solution, so there can only be complete ionisation when the solution is very dilute.—*Comptes Rendus*, cxliiii., No. 16.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, October 18th, 1906.

Prof. Sir WILLIAM RAMSAY, K.C.B., F.R.S., Foreign Secretary, in the Chair.

Presentation of the Longstaff Medal.

IN the absence of the President through illness, the following Address from him was communicated:—

The Longstaff Medal, as announced last Session, has been awarded to Prof. Walter Noel Hartley for his researches in Spectro-chemistry. It is over a quarter of a century since Hartley first entered this domain of physical chemistry which he has since cultivated with unremitting zeal and conspicuous success. To him belongs the distinct credit of being among the first to realise that valuable information concerning the constitution of chemical compounds might be obtained by the study of their absorption spectra, not only within the region of the visible spectrum, but, what is of far greater importance, in that ultra-violet region which is so easily dealt with by the photographic plate. His first contribution (in conjunction with Prof. Huntingdon) appeared in 1879, and must be regarded as the pioneer research which laid the foundation of all subsequent work in the systematic study of absorption spectra carried out by Hartley himself in conjunction with various collaborators or by independent workers inspired by the success of the method. The merits of this first memoir and of all the results which have followed from it consist not only in the establishment of the principle of a relationship between a particular optical property of a molecule and its chemical structure, but in the practical development of the methods by which this principle has been established. Setting out originally with the object of studying the ultra-violet absorption spectra of compounds of known constitution by means of the photographic plate, Hartley was soon compelled to turn his attention to emission spectra, and his well-known tin-lead-cadmium alloy was devised and used as a means of supplying spark spectra rich in ultra-violet lines of known wave-lengths. His later incursions into this field of spectroscopy are sufficiently well known. It is only necessary to refer to his spectrographic method of studying alloys and his researches on flame spectra and their applications to mineral analysis and to metallurgical processes. While there is no branch of spectro-chemistry which he has handled to which Hartley has not made valuable contributions, it is for the long series of researches on the relationship between absorption spectra and chemical constitution commencing in 1879 and continuing down to his latest communication published in last year's volume of our *Transactions* that the Longstaff Medal is more especially awarded. Although associated with many colleagues in the course of this work, the main source of inspiration has doubtless been Hartley himself. By his labours he has placed in the hands of chemists a method of studying chemical constitution which must for all time be taken into consideration. It is not only the method itself, but the mode of expressing the results by what he called "curves of molecular vibration" that first enabled chemists to realise the power of the new weapon. The continuous series of investigations proceeding from Hartley and his colleagues since 1879, and the more recent and no less important contributions now being made by other workers in the same field, all bear witness to the fertility of this spectroscopic method. An appeal to the more modern literature of the subject will show that not only has the original conception of the pioneer been amply justified, but that his methods have shown themselves capable of dealing with the more recondite problems of isomerism and tautomerism in its various aspects, and the relationship between colour and chemical constitution. It is perhaps safe to say that no discussion on this latter sub-

ject can lead to definite conclusions if absorption spectra be ignored.

In presenting the Longstaff Medal to Prof. Hartley it will doubtless be the unanimous desire of the Fellows of the Chemical Society that the presentation should be accompanied by the wish that he may long be spared to carry on that branch of physico-chemical work of which he is practically the founder, and with the development of which his name will always be honourably associated to the lasting credit of British Science.

The Longstaff Medal was then presented to Professor Walter Noel Hartley by the Chairman, and duly acknowledged.

Messrs. G. H. A. Clowes, B. Flurschheim, S. S. Pickles, H. Rogerson, and H. W. M. Willett were formally admitted Fellows of the Society.

The CHAIRMAN stated that on the occasion of the Jubilee of the Foundation of the Coal-tar Colour Industry celebrated in July, the following Address was presented to Sir William H. Perkin by the President:—

To WILLIAM HENRY PERKIN, LL.D., Ph.D., F.R.S.
From the Chemical Society.

Among those who congratulate you on the occasion of the celebration of the fiftieth anniversary of your discovery of the first Coal-tar Colour, the Chemical Society is not only aware of your great services to Chemical Science and Chemical Technology, but may claim to know you more intimately than any other body. Elected a Fellow in the year in which you began to manufacture Mauve, you are one of its oldest members; as one of its Secretaries during the years 1869-83, and as its President in 1883-85, you have rendered most valuable service in the conduct of its affairs; but it is chiefly for your many contributions to its *Proceedings* that it is indebted to you. Singularly consistent in your choice of the Society's publications as the means of making your work known, you have at all times been one of the chief supporters of its efforts to promote the progress of Chemical Science.

It is impossible to overrate the value directly and indirectly of your discovery; the evidence of the influence which it has exercised is overwhelming. And it is noteworthy that you should have been active not only at the beginning of the colour industry, but that you have more than once intervened to assist its progress; notably by the part which you took in the development of the manufacture of the Madder colours; by your work on Cinnamic acid which was of critical importance in the early stages of the development of the artificial indigo industry; and by your discovery of a method of producing Coumarin artificially which entitles you to rank as the pioneer in the establishment of an important offshoot of the colour industry, that of artificial perfumes.

The extraordinary progress of Chemical Science during the past half century indeed is in a very large measure the outcome of your discovery; had it not been proved to be a useful science, Chemistry would never have attracted the army of workers whose victories have led to the marvelous developments which are to be chronicled on every side. The advance of knowledge is little short of miraculous, especially in view of the difficulties with which chemists are confronted.

But however highly your technical achievements be rated, those who have been intimately associated with you must feel that the example which you have set by your rectitude as well as by your modesty and sincerity of purpose is of chiefest value. That you should have been able, as a very young man, to overcome the extraordinary difficulties incident to the establishment of an entirely novel industry fifty years ago, is a clear proof that you were possessed in an unusual degree of courage, independence of character, judgment, and resourcefulness; but even more striking is your return into the fold of scientific workers and the ardour with which you have devoted yourself to the prosecution of abstract physico-chemical

inquiries of exceptional difficulty. In the account of your renowned Master, Hofmann, you have stated that one of your great fears on entering into technical work was that it might prevent your continuing research work; that you should have felt such regret at such a period is sufficiently remarkable, and it must be a source of enduring satisfaction to you to know that your later scientific work deserves, in the opinion of many, to rank certainly no less highly than your earlier.

It is with a feeling of just pride that the Chemical Society now places on record its deep sense of the obligation which you have laid upon it by having won for British Chemical Science the incomparable distinction of making so great a step in the progress of civilisation as is marked by your discovery and its consequences.

Signed on behalf of the Chemical Society this Twenty-sixth day of July, 1906,

RAPHAEL MELDOLA, President.
ALEXANDER SCOTT, Treasurer.
M. O. FORSTER, | Honorary
ARTHUR W. CROSSLEY, | Secretaries.
WILLIAM RAMSAY, Foreign Secretary.

It was also announced that during the celebration by the University of Aberdeen of its Fourth Centenary, the following Address was presented in the name of the Society by the President:—

To the University of Aberdeen.

On behalf of the Chemical Society we beg to offer our most hearty congratulations to the University of Aberdeen on the occasion of the celebration of its Fourth Centenary. At an early period in its history the University gave prominence to Chemistry, and by so doing has rendered the greatest service to our Science as an educational subject. The University Chair of Chemistry has been filled successively by a number of distinguished men, Fellows of our Society, many of whom have extended the boundaries of Scientific Knowledge by their original investigations.

The inauguration of the new buildings will be regarded as marking the commencement of a new period of useful activity in the educational history of this country. The establishment of the new Laboratories will give the greatest satisfaction to English Chemists, as it is recognised that the improved facilities for instruction and research thus placed at the disposal of the University will insure the future development of their Science in Aberdeen, both as a branch of Academic Learning and as a subject of the greatest importance to the material welfare of the Nation.

In the name of the Council and Fellows of the Chemical Society we desire to place on record our most sincere wishes for the continued prosperity of the University of Aberdeen, both in our own Department of Scientific Knowledge and in all those studies which during the four past centuries it has fostered with such conspicuous success.

Signed on behalf of the Chemical Society this Twenty-sixth day of July, 1906,

RAPHAEL MELDOLA, President.
ALEXANDER SCOTT, Treasurer.
M. O. FORSTER, | Honorary
ARTHUR W. CROSSLEY, | Secretaries.
WILLIAM RAMSAY, Foreign Secretary.

Certificates were read for the first time in favour of Messrs. Paul Seidelin Arup, M.A., Marsden Villa, 62, Haverstock Hill, N.W.; Oscar Walter Betha, Meridian, Miss., U.S.A.; James Spears Broome, B.Sc., 18, Seedley Park Road, Pendleton, Manchester; Thomas Henry Byrom, 31, Wrightington Street, Wigan; John Carmichael, 10, Cortayne Road, Fulham, S.W.; Percy Henry Carpenter, A.I.C., 46, Streathbourne Road, Upper Tooting, S.W.; Charles Taylor Cockburn, 34, Queen's Gate, Dowanhill, Glasgow; Hubert Frank Coward, M.Sc., Hulme Hall, Plymouth Grove, Manchester; Archibald Prideaux Davson, A.R.C.S., 39, Blandford Square, N.W.; Anthony Nisbet Fitzgerald, B.A., B.Sc., 12, St. Mary's Road, Strood, Rochester; Octavius Hall, L.R.C.S.,

L.R.C.P., 6, Devonshire, Villas Plymouth; H. Norman Hanson, Field Head, Brighouse, Yorks; Charles Percy Hines, B.Sc., The Grammar School, Dartford; Edward Rees Jones, Llangedwyn Vicarage, Oswestry; William Richard Simpson Ladell, 19, Alwyne Road, N.; David McIntosh, B.Sc., Stamford School, Stamford; John Mastin, Woodleigh House, Totley Brook, nr. Sheffield; George Naylor, 45, Hornby Road, Blackpool; Charles Harold Oxland, B.Sc., 37, Waterloo Road, Bedford; Frederic Ion Richardson, B.A., Glenarbor, Kew, nr. Melbourne, Australia; Reginald Ernest Robinson, B.A., The Villas, Stoke-on-Trent; John Lionel Simonsen, M.Sc., 152, Barlow Moor Road, West Didsbury, Manchester; Charles Smith, Knowsley Road, Smithells, Bolton; Harry George Telling, Cooksbridge, Sussex; George Gordon Watt, 26, Albert Square, Clapham Road, S.W.; Chr. Winther, The University, Copenhagen.

Of the following papers, those marked * were read:—

*170. "*The Description and Spectrographic Analysis of a Meteoric Stone.*" By WALTER NOEL HARTLEY.

This stony meteorite was seen to fall in the Kangra Valley, Northern Punjab, in 1897, and was received in the same year from Lieut.-Col. Donald St. John Dundas Grant, of the India Medical Service. It consists of a crystalline stony base, throughout which are dispersed bright silvery metallic particles from 0.5 to 1 m.m. in diameter. The analysis was carried out according to the method previously described (Hartley and Ramage, *Trans.*, 1901, lxxix., 61). The principal constituents of the metallic portion are iron, nickel, cobalt, and chromium, with small quantities of copper, silver, lead, and gallium. Manganese, calcium, potassium, and sodium are present only in minute proportions. The chief components of the silicates other than silica are calcium and magnesium oxides. The bases present in minute proportions are iron, nickel, chromium, strontium, lead, silver, manganese, potassium, and sodium.

*171. "*Malacone, a Silicate of Zirconium containing Argon and Helium.*" By STANHOPE KITCHIN and WILLIAM GEORGE WINTERSON.

This mineral, found at Hitteroe and Arendal, Norway, is radio-active, and gives off a mixture of helium and argon when heated. As it is the only mineral from which argon has been obtained, a careful analysis was made with the object of seeing whether the presence of any unknown or unusual constituent would account for the presence of the argon. The analysis, discounting ferric oxide, uranium oxide, &c., points to the ratio $3\text{ZrO}_2 : 2\text{SiO}_2$ between the zirconia and the silica. The zirconia, converted into the basic chloride ZrOCl_2 and fractionally crystallised, was found to give the ratio 1:2 between the zirconium and chlorine, taking the atomic weight of zirconium at its accepted value, 90.

The mineral is feebly radio-active, and its radio-activity is considerably higher than that deduced from its content of uranium; but it still remains to make a careful examination of the nature of the emanation evolved, which, although it has a considerable period of decay, has not been proved to be identical with that from radium.

*172. "*The Relationship of Colour and Fluorescence to Constitution. Part I. The Condensation Products of Mellitic and Pyromellitic Acid with Resorcinol.*" By O. SILBERRAD.

Mellitic and pyromellitic acids condense with resorcinol to form compounds analogous to fluorescein.

Mellitic acid forms three series of products, namely, mono-, di-, and tri-xanthryl derivatives, of which the dixanthryl derivatives exist in two modifications, namely, meta and para. Pyromellitic acid forms mono- and dixanthryl derivatives. Representatives of all of these classes have been prepared.

One of the chief interests of the work lies in its bearing on the quinone theory of the structure of the phthaleins. Many of the compounds described do not admit of formulation on the quinone type, but are nevertheless intense

colouring matters and strongly fluorescent. The analogy between these compounds and the phthaleins is so close that it appears very probable that the latter also contain no quinone group.

Indications have also been obtained that the change from a lactonic structure to that of a carboxylic acid and *vice versa* does not take place with the ease which has generally been assumed; this also has an important bearing on the supposed tautomerism of the phthaleins.

The structure of the mellitins and pyromellitins follows in general from the method of preparation and the results of analysis. In the case of the dixanthryl derivatives, it was necessary to differentiate between the meta- and para-isomerides, by determining whether they were capable of further combining with resorcinol.

The following compounds, together with their potassium, lithium, ammonium, copper, lead, mercury, barium, cobalt, iron, and silver salts, were investigated.

3:6:9-Trihydroxyxanthrylbenzene-2-carboxylactone-4:5-dicarboxylic acid, together with its tetrabromo- and tetraiodo-derivatives.

3:3':6:6':9:9'-Hexahydroxy-m-dixanthrylbenzene-2:4:5:6-tetracarboxylic acid and its octobromo-derivative.

3:3':6:6':9:9'-Hexahydroxy-p-dixanthrylbenzene-2:3:5:6-tetracarboxylic acid.

3:3':3'':6:6':6'':9:9':9''-Nonohydroxy-sym-trixanthrylbenzene; 2:4:6-tricarboxylic acid, together with its dodecabromo- and dodecaiodo-derivatives.

*173. "Separation of $\alpha\alpha$ - and $\beta\beta$ -Dimethyladipic Acids." By ARTHUR WILLIAM CROSSLEY and NORAH RENOUF.

Experiments were described by which it has been found possible, contrary to the statement of Blanc (*Bull. Soc. Chim.*, 1905, [iii.], xxxiii., 879), to separate $\alpha\alpha$ - and $\beta\beta$ -dimethyladipic acids. The method depends on the different solubilities of these two acids in water saturated with hydrogen chloride, and in a mixture of chloroform and light petroleum.

*174. "Action of Alcoholic Potassium Hydroxide on 3-Bromo-1:1-dimethylhexahydrobenzene." By ARTHUR WILLIAM CROSSLEY and NORAH RENOUF.

Further investigation of 1:1-dimethyl- Δ^4 -tetrahydrobenzene (*Trans.*, 1905, lxxvii., 1499), prepared by the action of alcoholic potassium hydroxide on 3-bromo-1:1-dimethylhexahydrobenzene, has shown it to be a mixture of this hydrocarbon with the isomeric 1:1-dimethyl- Δ^4 -tetrahydrobenzene, in which the former always predominates.

This has been rendered possible by the discovery of a means of separating the oxidation products of these two substances, namely, $\alpha\alpha$ - and $\beta\beta$ -dimethyladipic acids.

*175. "The Conversion of Morphine and Codeine into Optical Isomerides." (Preliminary communication). By FREDERIC HERBERT LEES and FRANK TUTIN.

It was demonstrated by Schryver and Lees (*Trans.*, 1900, lxxvii., 1024, and 1901, lxxix., 563) that the chloro- and bromo-derivatives of morphine and codeine of the respective types $C_{17}H_{18}O_2N \cdot X$ and $C_{18}H_{20}N \cdot X$, prepared and described by them (*loc. cit.*), do not regenerate simply the original bases when they are hydrolysed by water. In every case a mixture of bases isomeric with the parent substance was produced, and of these isomorphine, β -isomorphine, and isocodeine were isolated and described. As isomorphine appeared to be the chief product of the action of water on bromomorphide (m. p. 170°) it was fully studied in order to obtain information respecting its relation to morphine. Of the two theories advanced respecting this relation, that of stereoisomerism was at the time considered to be the less probable.

From the consideration of the fact that Schryver and Lees demonstrated a complete chemical analogy between morphine and isomorphine (compare also Knorr and Hawthorne, *Ber.*, 1902, xxxv., 3010), and that the only differences between the bases are of a purely physical character and such as are found among optical isomerides, the present authors conclude that the isomerism must

without doubt be optical in character. Experimental evidence confirming this view has now been obtained.

Since the scope of the present investigation, on which the authors have been engaged for some time, has necessarily become extended to a study of the products of the hydrolysis of all the mono-halogen derivatives of morphine and codeine, they intended to delay publication until the whole subject was completed. The appearance, however, of a recent paper by R. Pschorr (*Ber.*, 1906, xxxix., 3130), entitled "Halogen Derivate von Morphin und Codein und deren Abbau," from which it is evident that the halogen derivatives obtained by Schryver and Lees are receiving attention, renders it desirable that the authors should publish some of their results and conclusions in order to indicate the lines on which they are still working.

Bromocodeine (m. p. 162°), on hydrolysis with water, gives an optically active mixture consisting, in unequal proportions, of bases isomeric with codeine. By fractionally crystallising the mixture from ethyl acetate and from alcohol, until products were obtained which showed no change in melting-point and specific rotatory power, the following substances were isolated:—

A-Base.—This formed slender prismatic needles melting at 145 — 145.5° , and had $[\alpha]_D -205^\circ$ in chloroform.

B-Base.—This formed colourless tabular prisms melting at 171 — 172° , and had $[\alpha]_D -155^\circ$ in chloroform.

When codeine is treated with excess of phosphorus tribromide in chloroform, the reaction is most vigorous, and bromination is almost immediately complete. When this solution is heated on a water-bath for a quarter of an hour, instead of for one hour, as was previously the case, the resulting bromo-derivative apparently contains less of the crystalline bromocodeine (m. p. 162°), and is a mixture. When this product is hydrolysed with water and the resulting mixture of isomeric codeines fractionally crystallised, codeine (m. p. 155° , $[\alpha]_D -122^\circ$) was isolated in addition to the above-mentioned A- and B-bases.

The substance described above as the B-base has now been shown to be isocodeine, the codeine analogue of isomorphine, for it is readily produced from the latter by methylation with sodium ethoxide and dimethyl sulphate. The isocodeine obtained by Schryver and Lees (*loc. cit.*) was apparently contaminated with a small proportion of the A-base.

The A-base, although undergoing no resolution by numerous crystallisations from several solvents, has been proved to be a molecular mixture of isocodeine (m. p. 171 — 172°) and a more highly levorotatory isomeride which has not yet been prepared in the pure state.

By the reactions mentioned, the authors have thus obtained conclusive evidence of the formation in unequal proportions of codeine and two other optically isomeric levorotatory bases.

These facts permit of the following conclusions respecting the constitution of morphine:—

1. The above-mentioned isomeric codeines are the result of the racemisation of two asymmetric carbon atoms in a molecule which must necessarily contain a third asymmetric system.

2. The carbon atoms which undergo racemisation are most probably those in the reduced phenanthrene nucleus to which the alcoholic hydroxyl group and the nitrogen atom are respectively attached. It follows from this that the latter carbon atom must necessarily be hydrogenised in order to be asymmetric.

3. The possible isomeric codeines produced by the racemisation of the two asymmetric carbon atoms must be represented by the configurations $++-$, $+-$, $-+-$, $---$, as at least three of them are levorotatory.

176. "The Aminodicarboxylic Acid derived from Pinene." By WILLIAM AUGUSTUS TILDEN and DONALD FRANCIS BLYTHER.

This is the acid originally obtained by Tilden and Burrows (*Trans.*, 1905, lxxvii., 344). In the present communication details are given for the preparation of the acid and its hydrochloride, nitrate, acid oxalate, copper salt,

ethyl ester, and its hydrochloride, and the acetyl derivative of the amino-acid.

Experiments are being continued on the products of the oxidation of the acid and of its condensation with benzaldehyde and glycocine.

177. "The Preparation and Properties of Dihydroxypinylamine (Pinocampophylamine)." By WILLIAM AUGUSTUS TILDEN and FREDERICK GEORGE SHEPHEARD.

Dihydroxypinylamine is the chief product of the reduction of nitrosopinene by means of boiling amyl alcohol and sodium. The free base is a colourless liquid having an odour like pinylamine, and boiling at 198—199°.

The hydrochloride, platinichloride, picrate, nitrate, oxalate, also the acetyl and benzoyl derivatives, and the carbamide, have been prepared and analysed. The alcohol obtained by the action of nitrous acid on the aqueous solution of the hydrochloride of the base boils at 103° under 15 m.m. pressure, and is identical with pinocampheol prepared by reduction of pinocampnone.

178. "Determination of Nitrates." By FRANK STURDY SINNATT.

Knecht and Hibbert's method for the estimation of picric acid (*Ber.*, 1903, xxxvi., 1549) may be applied to the estimation of nitrates.

The process depends on the conversion of the nitrate into picric acid by means of phenolsulphonic acid, the picric acid being subsequently estimated by titanium trichloride.

Up to the present the method has only been used for the estimation of re-crystallised pure potassium nitrate; it was carried out as follows:—

Ten c.c. of the solution of potassium nitrate containing 0.1 per cent of potassium salt were evaporated to dryness in a steam oven, 5 c.c. of a solution of phenolsulphonic acid added, and the heating continued for half-an-hour. The whole was then washed into a flask, and, after adding hydrochloric acid, titrated with titanium trichloride.

Three titrations carried out in the above manner required, for 0.01 grm. of potassium nitrate, 20.14, 20.47, and 20.2 c.c. of titanium trichloride (1 c.c. = 0.0004860 grm. of potassium nitrate), corresponding to 0.009788, 0.009948, and 0.009817 grm. of potassium nitrate respectively. The error is not so great as when the colorimetric method is used.

179. "The Nature of Ammoniacal Copper Solutions." By HARRY MEDFORTH DAWSON.

The nature and dissociation of the complex cupri-ammonia compound which is present in ammoniacal solutions of copper sulphate has been further examined. The method consisted in determining the amount of free ammonia in variously concentrated copper solutions containing different relative amounts of ammonia by extracting these solutions with chloroform. Special precautions have been taken with the view of obtaining accurate results, and a correction has been applied for the ammonia-displacing action of the dissolved salt. The experimental data indicate the existence in solution of a dissociating complex compound containing four molecules of ammonia per atom of copper. The ammonia dissociation increases with dilution, and, for a given copper concentration, with decrease in the relative proportion of ammonia. From experiments in which the free ammonia in ammoniacal copper sulphate solutions was determined by the method of gas-bubbling, Locke and Forssall (*Am. Chem. Journ.*, 1904, xxxi., 268) have drawn the conclusion that such solutions contain practically the whole of the copper in the form of a stable complex ion, Cu_4NH_3 . According to the author's observations, this view is quite untenable.

180. "The Colouring Matters of the Stilbene Group." (Part III.). By ARTHUR GEORGE GREEN and PERCY FIELD CROSLAND.

In previous communications (*Trans.*, 1904, lxxxv., 1424, 1432) it has been shown that the first action of caustic alkalis on *p*-nitrotoluenesulphonic acid is the production of

an unstable and easily oxidisable dinitrosostilbenedisulphonic acid.

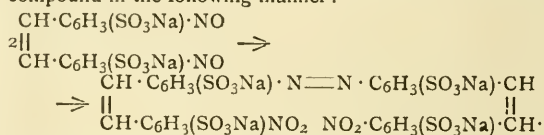
In order to study the subsequent transformation of this intermediate product by which dye-stuffs of the stilbene series are produced, typical colouring matters of this class, namely, stilbene yellow 8G and 4G, direct yellow, and Mikado orange, were submitted to examination by the following methods:—

A. Estimation of the quantity of hydrogen required to reduce the dye-stuff to diaminostilbenedisulphonic acid, employing for this purpose titration with standard titanium trichloride.

B. Estimation of the ethylene groups by determining the quantity of standard permanganate required to oxidise the dye-stuffs to aldehydes in cold dilute aqueous solution.

C. Isolation and characterisation of the aldehydes formed.

The results obtained agree with the assumption that in the second stage of transformation condensation takes place between two molecules of the intermediate dinitroso-compound in the following manner:—



The dinitroazodistilbenedisulphonic acid thus produced represents the structure of the greenest yellow of the series. The redder yellows and oranges are formed therefrom by the reduction of the two nitro-groups, first to an azoxy- and finally to an azo-group. The stilbene yellows 8G and 4G were proved to consist almost entirely of sodium dinitroazodistilbenedisulphonate. Direct yellow is less pure, but appears to consist substantially of sodium azoxyazodistilbenedisulphonate. Mikado orange, which could not be obtained entirely pure, gave results which approximate to those required for the diazostilbenedisulphonate.

It appears, therefore, that all the dye-stuffs of the stilbene series are true azo-compounds. Their chromophor being an azo-group, their dyeing properties are now satisfactorily explained. They differ, however, from most other azo-dye-stuffs in the entire absence of auxochrome groups.

181. "Interaction of Succinic Acid and Potassium Dichromate. Note on a Black Modification of Chromium Sesquioxide." By EMIL ALPHONSE WERNER.

When a mixture of finely-powdered potassium dichromate (1 mol.) and succinic acid (6 mols.) is heated, interaction takes place a few degrees above the boiling-point of the acid (181°). A compound having the composition $\text{Cr}_4(\text{C}_4\text{H}_4\text{O}_4)_5\cdot 7\text{H}_2\text{O}$ is formed, which has not the properties of a chromo-organic acid. It is practically insoluble in water, and on ignition in air leaves a residue of chromium sesquioxide which is black. The chromium hydroxide produced from it by decomposition with sodium hydroxide also leaves a jet-black modification of the sesquioxide after ignition.

182. "Derivatives of Polyvalent Iodine. The Action of Chlorine on Organic Iodo-derivatives, including the Sulphonium and Tetra-substituted Ammonium Iodides." By EMIL ALPHONSE WERNER.

Experiments have been made with the object of ascertaining if organic iodo-compounds other than the immediate derivatives of benzene and its homologues can form addition compounds with chlorine corresponding to the iodoso-chlorides.

Iodothiophen, $\text{C}_4\text{H}_3\text{IS}$ (S:I = 1:2), and di-iodothiophen, $\text{C}_4\text{H}_2\text{I}_2\text{S}$, m. p. 40°, behave like open-chain compounds; on the other hand, tetraiodopyrrole, $\text{C}_4\text{NH}\cdot\text{I}_4$, forms the additive compounds $\text{C}_4\text{NH}\cdot\text{I}_4\text{Cl}_4$ and $\text{C}_4\text{NH}\cdot\text{I}_4\text{Cl}_3$ (m. p. 158°).

A few new iodoso-derivatives of benzene have been prepared. By the action of chlorine on the sulphonium and

tetra-substituted ammonium iodides, compounds of the type $\text{RCI} \cdot \text{ICI}_3$ have been obtained, from which the more stable compound of the general formula $\text{RCI} \cdot \text{ICI}$ can be produced either by the action of heat or by treatment with a solution of sodium hydroxide.

The following compounds were described and their constitution discussed.

$(\text{CH}_3)_3\text{SCI} \cdot \text{ICI}_3$ and $(\text{CH}_3)_3\text{SCI} \cdot \text{ICI}$ (m. p. 103°).
 $\text{C}_2\text{H}_5(\text{C}_3\text{H}_7)_3\text{NCl} \cdot \text{ICI}_3$ and $\text{C}_2\text{H}_5(\text{C}_3\text{H}_7)_3\text{NCl} \cdot \text{ICI}$ (m. p. 94°).
 $(\text{C}_2\text{H}_5)_3\text{C}_5\text{H}_5\text{NCl} \cdot \text{ICI}_3$ and $(\text{C}_2\text{H}_5)_3\text{C}_5\text{H}_5\text{NCl} \cdot \text{ICI}$ (m. p. 35°).
 $(\text{CH}_3)_4\text{NCl} \cdot \text{ICI}$ (m. p. 217°) and $(\text{C}_2\text{H}_5)_4\text{NCl} \cdot \text{ICI}$ (m. p. 98°).

183. "The so-called 'Benzidine Chromate,' and Allied Substances." By JAMES MOIR.

This remarkable substance, which resembles cærulignone very closely, resulted on mixing solutions of benzidine and chromium trioxide. The author finds that it is the chromate, not of benzidine, but of a complex oxidation product of the latter, which has apparently the formula $\text{C}_{60}\text{H}_{46}\text{N}_{16}$. It behaves like cærulignone towards sulphuric acid and towards sulphites, giving an intense crimson coloration with the former, and yielding *benzidine-2-monosulphonic acid* with the latter. The colour-base, $\text{C}_{60}\text{H}_{46}\text{N}_{16}$, appears to have resulted from the condensation of three molecules of diphenylquinone-di-imine (*Ber.*, 1905, xxxviii., 1232) with two of benzidine, in somewhat the same manner as dianilinoquinonedianil arises from quinone and aniline. On treating with ammonia, only one molecule of benzidine separated from the C_{60} complex, and by the action of potassium sulphite, three molecules of benzidinesulphonic acid were produced. "Benzidine chromate" contains four molecules of chromic acid, but the author has also prepared a substance containing nearly twice as much chromium, which is either $\text{C}_{60}\text{H}_{46}\text{N}_{10} \cdot 2\text{H}_2\text{Cr}_4\text{O}_{13}$ or merely diphenylquinone-di-imine sesquichromate, $\text{C}_{12}\text{H}_{10}\text{N}_2 + 1\frac{1}{2}\text{CrO}_3$.

By heating 3:3'-dibromo-5:5'-tolidine with chromic acid, a green homologue of "benzidine chromate" was obtained. Its analysis agrees with the formula $\text{C}_{60}\text{H}_{28}(\text{CH}_3)_{10}\text{N}_{10}\text{Br}_8 + 9\text{H}_2\text{CrO}_4$, which would be expected from the constitutional formula put forward by the author for "benzidine chromate."

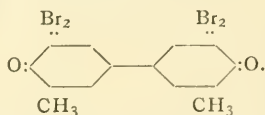
The "ferricyanide of benzidine" has also been investigated. It is similar to and contains the same colour-base as the "chromate," having the formula $\text{C}_{60}\text{H}_{46}\text{N}_{10} + 2\text{H}_3\text{Fe}(\text{CN})_6$. The action of ammonia resulted in the separation of very little benzidine, giving chiefly another dark colour base and ammonium ferricyanide.

184. "New Derivatives of Diphenol 4:4'-Dihydroxydiphenol." By JAMES MOIR.

By the sulphonation of diphenol the author has prepared the 3:3'-disulphonic acid, the 3:5:3'-trisulphonic acid, and the 3:5:3':5'-tetrasulphonic acid.

With chlorosulphonic acid, diphenetole yielded (a) 4:4'-diphenetole-3-sulphonic acid, (b) 4:4'-diphenetole-3:3'-disulphonic acid, and (c) an indifferent substance containing chlorine and sulphur.

On brominating Schütz's dinitrodiphenol, a *dibromodinitrodiphenol* melting at 237° was obtained, and from dicresol the 5:5'-*dibromodicresol* melting at 185° was prepared; this combines with excess of bromine to form a scarlet substance analogous to tribromophenol bromide, and possessing the constitution—



The *dibenzoate* of diphenol prepared by the Schotten-Baumann method melts at 241° .

185. "On the Interaction of the Alkyl Sulphates with the Nitrites of the Alkali Metals and Metals of the

Alkaline Earths." By PRAFULLA CHANDRA RAY and PANCHANAN NEOGI.

By the interaction of the sodium, potassium, barium, and calcium salts of ethyl sulphuric acid and the nitrites of the alkali metals and metals of the alkaline earths, both ethyl nitrite and nitrothane were formed. In the case of potassium ethyl sulphate and potassium or sodium nitrite, small quantities of nitrobutane were also obtained.

186. "The Electrolytic Preparation of Dialkyldisulphides." (Preliminary Note). By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

By the electrolysis of a concentrated aqueous solution of ethyl sodium thiosulphate, commonly known as Bunte's salt (*Ber.*, 1874, vii., 646), diethylsulphide is formed at the anode, and separates as an oily liquid on the surface of the electrolyte. The electrolysis was carried out in a beaker, the cathode consisting of a sheet of platinum-foil lying close to the sides of the beaker, the anode being a piece of stout platinum-wire. The solution contained a quantity of sodium bicarbonate equivalent to the Bunte's salt taken, otherwise the disulphide was decomposed by the sulphuric acid formed during electrolysis, giving the mercaptan. The current density at the anode was 100 ampères per sq. c.m., and the yield was more than 50 per cent of the theoretical. The disulphide obtained distilled almost completely at 152° . It forms a compound with silver nitrate, which, on analysis, gave $\text{Ag} = 36.93$. $(\text{C}_2\text{H}_5)_2\text{S}_2 \cdot \text{AgNO}_3$ requires $\text{Ag} = 36.95$ per cent.

Similar results were obtained by electrolysis solutions of benzyl sodium thiosulphate (Purgotti, *Gazzetta*, 1890, xx., 24), dibenzylsulphide being produced in a yield of more than 80 per cent; this was crystallised from alcohol, and melted at 70° . Analysis of the compound with silver nitrate gave $\text{Ag} = 26.3$. $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{S}_2 \cdot \text{AgNO}_3$ requires $\text{Ag} = 26.0$ per cent.

This reaction is being more thoroughly investigated and extended to the preparation of other disulphides.

187. "The Direct Union of Carbon and Hydrogen at High Temperatures." By JOHN NORMAN PRING and ROBERT SALMON HUTTON.

Previous work has been limited to a study of this reaction at 1200 – 1350° and to the investigation of the products obtained when a carbon arc is maintained in hydrogen. The authors have now supplemented these observations by working at intermediate temperatures.

For this purpose, a special form of apparatus was devised in which carbon rods, supported at the centre of a glass or metal vessel containing hydrogen, were heated to any desired temperature by the resistance which they offer to the passage of an electric current. By carrying out experiments at gradually increasing temperatures, it was found that traces of acetylene were already formed at 1700° , and the percentage of acetylene increased fairly uniformly with the temperature up to 2800° , which was the maximum point attained. The production of acetylene at these comparatively low temperatures, and independently of any of the complicated electrical phenomena which accompany the arc, does not seem to have been noted previously.

The formation of methane was also carefully studied at temperatures from 1000° upwards; the amounts found were in most cases much below those indicated by Bone and Jerdan (*Trans.*, 1897, lxxi., 41; 1901, lxxix., 1042), and seemed to diminish as the purity of the carbon increased.

188. "The Action of Nitrogen Sulphide on certain Metallic Chlorides." By OLIVER CHARLES MINTY DAVIS.

When nitrogen sulphide dissolved in dry chloroform is added to the tetrachlorides of tin and titanium, the pentachlorides of antimony and molybdenum, and also tungsten hexachloride dissolved in the same solvent, interaction readily takes place. With stannic chloride, antimony pentachloride, and molybdenum pentachloride, the compounds formed are represented by the formulae $\text{SnCl}_4 \cdot 2\text{N}_4\text{S}_4$, $\text{SbCl}_5 \cdot \text{N}_4\text{S}_4$, and $\text{MoCl}_5 \cdot \text{N}_4\text{S}_4$ respectively, but the chlorides of tungsten and titanium are first reduced before combining

with nitrogen sulphide, finally giving compounds having the formulæ WoCl_4 , N_4S_4 and Ti_2Cl_6 , N_4S_4 . These substances are decomposed on exposure to moist air with varying degrees of rapidity, and less readily when preserved beneath dry chloroform. Negative results were obtained with the trichlorides of iron, antimony, and arsenic.

189. "The Determination of Halogen." By JAMES MOIR.

The substance to be analysed having been weighed directly into a tall nickel crucible, ten drops of water and five to seven "pastilles" of pure potassium hydrate are added, and the mixture is stirred with a platinum-wire while it is heated on the steam-bath; when it is uniform, from 0.5 to 1 grm. of finely-powdered potassium permanganate is stirred in, in small portions at a time; the mixture is then heated on the steam-bath until dry, being watched in case frothing occurs; it is afterwards heated slowly to visible redness or until the glowing caused by the interaction between separated carbon and manganese dioxide is over. The cool crucible is placed in a warm dilute solution of potassium bisulphite; the solution is then carefully acidified with acetic acid and filtered directly into a solution of silver nitrate. The silver halide may be worked up with nitric acid in the usual manner, or the cooled crucible may be placed in water and the solution carefully acidified with acetic acid until the manganate is converted into permanganate; the latter is then destroyed by means of barium dioxide, the filtered solution neutralised with sodium bicarbonate and titrated, using chromate as indicator.

PHYSICAL SOCIETY.

Ordinary Meeting, October 26th, 1906.

Prof. J. PERRY, F.R.S., President, in the Chair.

A PAPER on "The Strength and Behaviour of Ductile Materials under Combined Stress" was read by Mr. W. A. SCOBLE.

In former tests of materials under combined stress either the ultimate strength or elastic limit stress has been considered, and the tensions have been applied either directly, or by internal pressure in the case of thin tubes, so that the distribution of stress was approximately uniform. The present experiments were made on bars $\frac{3}{4}$ inch diameter, subjected to bending and twisting to reproduce the irregular distribution of stress occurring in practice. The yield-point was selected as the criterion of strength, but it is open to more than one specification. Here the stress corresponding to the first sign of yield was not taken, but that given by the intersection of the two parts of the stress-strain diagram corresponding to perfect elasticity and complete yield, so that the intermediate state was neglected. The critical bending moment was found to be greater than the yield torque, 2660 and 2400 lbs. ins., and plotting the corresponding bending and twisting moments the ellipse gave the closest approximation to the results. The circular formula $M_e = T_e = \sqrt{M^2 + T^2}$ may be used, taking M_e and the tensile strength if the torque is small, or T_e and the working torsional shear-stress if the bending moment is small. With both loads on, there was simultaneous yielding in both ways. The maximum principal stress varied considerably, but the maximum shear stress was nearly constant. Usually the bar yielded in the manner corresponding to the fixed load before giving it that due to the increasing load; sometimes the difference in the loads was rather large. The results, together with those of other experiments, were analysed to determine if the variation of the maximum shear stress was due to a force analogous to friction, or the reverse, proportional to the force perpendicular to the plane of maximum shear. It was found that the variation in the values was due to differences in the shear strength in various directions.

Dr. MORROW, in a letter to the Secretary, remarked that he had read Mr. Scoble's paper with great interest,

and hoped it would help in removing the obstacles to the application of some theoretical formulæ in design. It was well known that many of the applications of the theory of bending were worse than useless in practice. In cases of combined tension and bending of solid bars (as in crane-hooks, coupling-rods of locomotives, &c.) the usual methods were misleading. In *Proc. Roy. Soc.*, vol. lxxiii., he (Dr. Morrow) described experiments showing that the strains, and hence probably also the stresses, caused by bending rectangular beams were considerably smaller than those given by calculation. Since then the method has been extended to higher stresses in wrought iron and steel bars, but still within the elastic limit. Direct measurements of the longitudinal tensile and compressive strains bear out the previous conclusions. Until it is realised that the ordinary theory of bending is inapplicable to materials of construction (except as a useful approximation when the stresses are low) it will be difficult to arrive at correct conclusions in any problem of combined stress in which bending occurs. Taking some of the results from Mr. Scoble's paper, in which failure was by bending, and assuming that the tensile stress was only $\frac{1}{2}$ of that given by the Euler-Bernoulli theory, Dr. Morrow has drawn up a table which shows that there is nothing to disprove the maximum principal stress theory when the specimen fails by bending. The method adopted is exceedingly rough and does not apply to the very different cases in which failure is by torsion or shearing.

The CHAIRMAN said the paper was a most valuable one, and more scientific experiments upon the subject were required. He could not agree with the notion put forward in many English test-books that the maximum principal stress determined fracture.

A paper by Mr. J. M. BALDWIN on "The Behaviour of Iron under Weak Periodic Magnetising Forces" was read by Prof. F. T. TROUTON.

The behaviour of iron in strong alternating fields has been studied by many observers, and the induction in iron when placed in both strong and weak fields has been thoroughly examined by static methods, but up to the present no results have been published of the induction in weak alternating fields. The Author has now, however, succeeded, by means of Lyle's Wave-Tracer (for description of which see *Phil. Mag.*, vol. vi., p. 549), in examining the induction in periodically varying fields down to extremely low amplitudes. The results are in general agreement with what might have been anticipated from work already done by Lord Rayleigh and others in weak fields by static methods, at least as far as such results can be extended to periodic fields. The method which was used may be shortly described as one in which the wave-curve of the induction is determined by examining the E.M.F. in a secondary coil by means of a commutator arrangement working on the same shaft as a dynamo supplying the primary current to a coil placed on the specimen to be examined. The principal points brought out by Mr. Baldwin's work are as follows:—(1) The permeability satisfies a linear law through a considerable range for weak fields, diminishing to a minimum about 150 as the amplitude of the field diminishes; (2) as the field diminishes the difference in phase between the induction and the magnetising force tends to disappear; and (3) at the same time the hysteresis losses become very small; (4) frequency at these low values of the field has practically no influence on the results obtained.

The CHAIRMAN expressed his interest in the paper and said that twelve or fourteen years ago he worked at the subject in connection with choking-coils, not kinetically, but using the ordinary hysteresis curves. Taking a periodic voltage applied to a choking-coil, it was interesting to note that the iron manufactured harmonics whose frequencies were the odd multiples of the frequency of the fundamental. He contrasted this with the case of trains of mechanism where the frequencies manufactured were always octaves or double octaves of the original frequency.

A paper by Prof. R. W. Wood on "*Fluorescence and Magnetic Rotation Spectra of Sodium Vapour and their Analysis*" was taken as read.

After recapitulating the descriptions of the experimental arrangements given in previous papers, the author describes the work done during the present year in photographing magnetic rotation and fluorescent spectra. A 12-foot grating, a specially constructed three-prism spectrograph, and a monochromatic illuminator were used. The sources of light employed were:—Quartz arc-lamps, containing cadmium, zinc, and thallium; ordinary arcs between lead, zinc, silver, bismuth, and copper electrodes; lithium, sodium, and barium arcs; and vacuum tubes containing helium and hydrogen. After each exposure the D lines were recorded on the photographic plate for purposes of comparison. Some observations on the fluorescence produced by cathode rays are also described. Details are given of the difficulties and special features of the spectra obtained, and directions are indicated for future work.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 15, October 8, 1906.

Succinic Pinacone.—Louis Henry.—The author investigates the methods by which succinic pinacone, $(\text{H}_3\text{C})_2\text{C}=\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-(\text{CH}_3)_2$, is prepared, and

finds that the easiest method—the one with the best yield—is by the reaction of magnesium methylbromide, $\text{H}_3\text{C}.\text{Mg}.\text{Br}$, on ethyl levulate, $\text{H}_3\text{C}-\text{CO}.\text{CH}_2.\text{CH}_2.\text{CO}(\text{OC}_2\text{H}_5)$. He then investigates its properties, and finds it to be a tertiary alcohol in two senses and contains the two components,

$-\text{C}(\text{OH})$, in the γ -position separated by a bicarbonate system, $-\text{C}-\text{C}-$. When heated, it partially dehydrates, a non-saturated tertiary alcohol resulting, of formula $(\text{H}_3\text{C})\text{C}=\text{CH}-\text{CH}_2-\text{C}(\text{CH}_3)_2$.

Liquefaction of the Starch of Grains.—A. Boidin.—The author continues his investigation on the influence of phosphates on the viscosity of starch, and he applies his results to the industry of distillation. The amyl matters are heated with the necessary quantity of acid to convert the alkaline polybasic phosphates into monobasic phosphates, and the fluid starch thus obtained is saccharified by the addition of a small quantity of saccharifying medium.

No. 16, October 15.

Chemical Functions of Textiles.—Léo Vignon.—The author has already shown that if silk, linen, and cotton are immersed in alkaline, acid, or saline liquors of known composition, placed in a calorimeter, certain constant and measurable thermic phenomena take place. The numbers show that linen and silk possess acid and basic functions, whilst cotton only has very slight acid functions. The author's further researches prove:—(1) That animal textiles have acid and basic chemical functions; (2) that vegetable textiles have no basic functions and possess comparatively feeble acid functions; (3) that porous bodies, as pulverised wood carbon, are inert from a chemical point of view. He also finds that the acid or basic chemical activity of textiles increases with the dilution of the aqueous solution.

Condensation of Acetylenic Nitriles with Amines. General Method of Synthesis of β -Substituted β -Amino-substituted Acrylic Nitriles.—Ch. Moureu and I. Lazennec.—The acetylenic nitriles, $\text{R}-\text{C}\equiv\text{C}-\text{CN}$, unite directly with the primary and secondary amines, giving β -substituted β -amino-substituted acrylic nitriles, $\text{R}-\text{C}=\text{CH}-\text{CN}$.

These are neutral bodies, easily hydrolysed by acids, with formation of β -ketonic nitriles, $\text{R}-\text{CO}-\text{CH}_2-\text{CN}$, and regeneration of the amines. This indirect method of fixation of water on to the acetylenic liaison is new and very curious. The authors propose to generalise it.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th inst., The Duke of Northumberland, K.G., President, in the Chair. The Special Thanks of the Members were returned to Dr. Albert P. Brubaker for his present of a portrait of the late Dr. Tyndall, and to Mr. Hugh Spottiswoode for a gift of apparatus.

Royal Society.—Award of Medals.—The Royal Society's Medals have this year been adjudicated by the President and Council as follows:—The Copley Medal to Professor Elias Metchnikoff for the importance of his work in zoology and in pathology; the Rumford Medal to Professor Hugh Longbourne Callendar for his experimental work on heat; a Royal Medal to Professor Alfred George Greenhill for his contributions to mathematics, especially the elliptic functions and their applications; a Royal Medal to Dr. Dukinfield Henry Scott for his investigations and discoveries in connection with the structure and relationships of fossil plants; the Davy Medal to Professor Rudolf Fittig for his investigations in chemistry, and especially for his work in lactones and acids; the Darwin Medal to Professor Hugh de Vries on the ground of the significance and extent of his experimental investigations in heredity and variation; the Hughes Medal to Mrs. W. E. Ayrton for her experimental investigations on the electric arc, and also upon sand ripples. The King has been graciously pleased to approve of the award of the Royal Medals. The Medals will, as usual, be presented at the Anniversary Meeting on St. Andrew's Day (Nov. 30). The Society will dine together at the Whitehall Rooms on the evening of the same day.

MEETINGS FOR THE WEEK.

TUESDAY, 13th.—Faraday Society, 8. "Investigations Relative to the Depreciation of Electrolytically produced Solutions of Sodium Hypochlorite," by W. P. Digby. "The Hermite Electrolytic Process at Poplar," by C. V. Biggs. "Electro-chemistry of Lead," by A. C. C. Cumming.

THURSDAY, 15th.—Chemical, 8.30. "Determination of the Rate of Chemical Change by Measurement of Gases Evolved," by F. E. E. Lamplough. "Xanthoxalanil and its Analogues," by S. Ruhemann.

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THE COMPOSITION OF THORIANITE, AND THE RELATIVE RADIO-ACTIVITY OF ITS CONSTITUENTS.*

By E. H. BÜCHNER, Ph.D.

Prefatory Note by Sir William Ramsay.

WHEN the cubical mineral from Ceylon, sent to me by Mr. Holland in December, 1903, and named by Professor Dunstan "Thorianite," was analysed by several of my students, it was evident that although in the main—as shown by the analysis made by Dr. T. A. Henry under Professor Dunstan's supervision—it consisted of the oxides of thorium and uranium, its composition is by no means simple. The analyses referred to were made by Dr. R. D. Denison, by Mr. Gimmingham, and by Mr. Le Rossignol; they are given in Table I. (for convenience of reference Dr. Henry's analyses are also appended).

The extraction of radiothorium by Dr. O. Hahn, "*Jahrb. f. Radioaktivität*," 1905, vol. ii., and various other investigations carried on in my laboratory, made it evident that under the heading "lead," for example, various other metals were included, and Dr. Büchner undertook to carry out an analysis on a larger amount, so as to ascertain what elements were present in the analytical groups into which the constituents of the mineral had been roughly divided by previous analysts. Another of the objects of his research was to determine how the radio-activity of thorianite is distributed over its various constituents. Assuming, as looks more than probable, that the radio-active constituents of thorianite, like those of similar radio-active minerals, are in process of change, it is to be expected that by working on comparatively large quantities, these bodies and their products can be identified, even though in themselves they may not display the property of radio-activity.

The methods employed in the chemical analysis of thorianite, together with the results obtained, will form the first section of this account, and the second part will deal with experiments relating to the radio-activity of the several fractions into which the mineral was separated.

The total quantity of mineral taken for analysis was 24.373 grms. On treatment with concentrated boiling nitric acid the greater part of it dissolved. After decantation, the residue was once more boiled with fresh acid, and only a small quantity remained insoluble. The solutions were then mixed, evaporated to dryness, heated to 130° to render any silica present insoluble, and re-dissolved in dilute hydrochloric acid. The residue, which was dried, ignited, and weighed, was non-volatile on treatment with hydrofluoric and sulphuric acids; on testing it, it proved to be zirconium oxide, which had separated out as a basic salt.

Sulphuretted hydrogen was then passed through the hot liquid; the precipitated sulphides were treated with a solution of sodium sulphide, in which a portion dissolved. The residue dissolved almost completely in dilute nitric acid, only a trace remaining, which was soluble in aqua regia; after excess of acid had been removed by evaporation it was dissolved in water, and could be re-precipitated by sulphuretted hydrogen. Its amount, however, was too small to prove undoubtedly that it was mercuric sulphide; mercury, however, has been found (by Miss Evans) in residues from a larger amount of mineral.

Sulphuric acid was added to the nitric acid solution, and the precipitated lead sulphate was filtered off, dried, and weighed.

Ammonia was then added to the filtrate; this should have precipitated bismuth as hydroxide; the colour of the precipitate, however, was reddish brown, and it was practically insoluble in hydrochloric acid; its quantity was also too small to permit of further investigation.

Copper was then precipitated by Rivot's method by addition to the filtrate of ammonium sulphocyanide, after reduction with sulphurous acid. The filtrate from the cuprous sulphocyanide gave traces of a brown precipitate with sulphuretted hydrogen, not in the least resembling cadmium sulphide.

The solution of the sulphides in sodium sulphide, which should have contained arsenic, antimony, and tin, and other elements capable of forming sulpho-salts, was analysed according to the methods of Bunsen and Clarke. A large excess of sulphurous acid was added to the liquid, and it was boiled for a long time. Arsenic is dissolved, antimony and tin remain behind. The insoluble residue was then suspended in water; ammonium persulphate and oxalic acid were added, and sulphuretted hydrogen was once more passed through the solution. After a repetition of this operation, the solution should have contained only antimony, and the residue, tin. The antimony sulphide, after excess of sulphur had been removed by carbon disulphide, had an almost black colour, probably due to the presence of selenium, which has been discovered by Professor Ogawa in this laboratory, in course of work on larger quantities of residue.

The solution, which was supposed to contain arsenic, was treated with sulphuretted hydrogen; to the precipitate, after solution and oxidation, ammonia and magnesia mixture were added, but no arsenate came down. On passing sulphuretted hydrogen, however, a small quantity of a black substance was precipitated.

To the filtrate from the sulphuretted hydrogen group ammonia was added after oxidation. The precipitate was re-dissolved in hydrochloric acid, and, after adding a little concentrated nitric acid, a solution of oxalic acid was poured into the solution. The oxalates of the rare earths separated in a granular state, and were separated by filtration. This precipitate was then treated, according to Brauner's method, with a solution of 20 grms. of ammonium oxalate in 40 grms. of water, and boiled for about ten minutes; the liquid was then diluted with about 800 c.c. of water. The thorium remains in solution; the ceria, &c., are precipitated. This process was repeated, and the solution was then evaporated to dryness and ignited; the thorium oxide was then weighed. The original solution in hydrochloric acid, however, still contained thorium and cerium; it was, therefore, partly evaporated and neutralised with ammonia, and oxalic acid was again added; the precipitate obtained was treated in the same way as has been already described. No attempt was made to separate ceria from the other earths, though they were present, as is proved by the red-brown colour of the Ce_2O_3 .

The ammonia group further contained iron, aluminium, and uranium, which are not precipitated by oxalic acid. They were separated by the usual methods; if the solution contains excess of ammonium carbonate, only iron and aluminium are precipitated by ammonium sulphide, and uranium is left in solution; after precipitation by evaporation, and re-solution in dilute hydrochloric acid, it was thrown down by ammonium hydroxide and weighed as U_3O_8 . The aluminium and iron were separated by treatment with excess of caustic potash.

The filtrate from the ammonia group was evaporated to dryness in a platinum basin, and the ammonium salts were expelled; the residue dissolved almost entirely in hydrochloric acid (residue w ; see experiments on radio-activity). After neutralisation of the excess of hydrochloric acid, calcium oxalate was precipitated; the filtrate was again evaporated, and heated to redness. A residue was left,

* A Paper read before the Royal Society, November 8, 1906.

TABLE I.

	Denison.	Gimingham.	Le Rossignol.	Dunstan and Henry.		
				1.	2.	3.
Thorium oxide, ThO ₂	76.4	77.52	77.07	72.24	76.22	78.86
Cerium oxide, Ce ₂ O ₃ ?				{ 6.39 }	8.04	1.02
Lanthanum oxide, La ₂ O ₃				0.51		
Didymium oxide, Di ₂ O ₃						
Uranium oxide, U ₃ O ₈	14.9	13.23	12.95	11.19	12.33	15.10
Ferric oxide, Fe ₂ O ₃	6.1	2.79	2.77	1.92	0.35	0.46
Lead oxide, PbO	2.0	3.42	2.41	2.25	2.87	2.59
Calcium oxide, CaO	—	—	—	—	—	1.13
Zirconium oxide, ZrO ₂	—	—	—	3.68	—	—
Loss on ignition	— (a)	1.63	1.63	—	—	0.20
Helium, He	—	—	—	—	—	0.39
Residue on fusion with H ₂ SO ₄ ..	0.7	2.02	2.60	0.41	0.12	—
	100.1	100.61	99.43	98.59	99.93	99.75

(a) Ignited mineral analysed.

TABLE II.

	Per cent.	Total activity.	Activity per 10 m.grms.	Activity (mineral = 100).		
Soluble Portion.						
HgO	Traces	284	Not weighed			
PbO.. .. .	2.42	{ 7206 (Feb. 6) 8360 (Feb. 27) 9570 (March 23)	{ 125 145 166 }	1.9	2.2	2.5
CuO.. .. .	0.08	10				
SnO ₂	0.05	None				
Sb ₂ O ₄	0.11	16				
Bi ₂ O ₃ ?	0.21	2153	{ 414 (Feb. 8) 421 (March 24) }	—	0.6	
As ₂ O ₃ ?	Traces	72				
CdO ?	Traces					
Fe ₂ O ₃	2.05	{ 17,530 (Feb. 13) 21,380 (March 5)	{ 351 428 }	4.6	5.7	
Al ₂ O ₃	0.15	None				
U ₃ O ₈	13.12	{ 24,915 (Feb. 15) 35,490 (April 6)	{ 78 111 }	6.6	9.4	
ThO ₂	70.96	216,190	125		57.2	
Ce ₂ O ₃	1.96	{ 8680 (Feb. 16) 9650 (March 28)	{ 178 198 }	2.3	2.6	
ZrO ₂	0.23	924	{ 165 (Feb. 8) 163 (March 28) }		0.2	
CaO.. .. .	0.13	{ 1080 (Feb. 14) 1225 (March 27)	{ 343 388 }	0.3	0.3	
Residue	1.50	6590	—		1.8	

Insoluble Portion.

HgO	Traces	49				
Bi ₂ O ₃ ?	0.15	124	44 and 16 (a)			
CdO?	Traces					
Fe ₂ O ₃	1.30	{ 664 (Feb. 13) 1010 (March 13)	{ 21 32 }	0.2	0.3	
Al ₂ O ₃	0.06	None				
U ₃ O ₈	0.02	21	40			
ZrO ₂	Traces					
TiO ₂	0.45	None				
Unknown substance	0.040	66				
P ₂ O ₅	Traces	None				
CO ₂	0.10					
He	0.15					
H ₂ O	3.20					
	98.84			75.7	80.3	

Original mineral 155
Standard uranium oxide 186

(a) This precipitate came down in two portions, which were filtered off and kept separate; the first had the smaller activity.

which was weighed, and submitted to several tests. Part of it dissolved on boiling with concentrated hydrochloric acid; the solution was evaporated, diluted with water, and treated with excess of caustic soda; the resulting precipitate was soluble in hydrochloric acid. After neutralisation, sodium phosphate gave a white precipitate (ϕ); on addition of ammonia to the filtrate, another precipitate came down in very small quantity (magnesia). The solution, which contained excess of soda, was evaporated and heated; on dissolving in water, a residue was left, soluble in hydrochloric acid, and precipitable by hydrogen sulphide with a brownish red colour. None of these precipitates have been investigated more closely.

The portion of the mineral, insoluble in nitric acid, was fused with hydrogen potassium sulphate; the fused mass dissolved almost completely in hot water; on addition of a little hydrochloric acid, however, a precipitate was formed. After this had been removed by filtration, a further quantity of a white substance separated. Sulphuretted hydrogen was passed through the filtrate from this second precipitate, when a red-brown precipitate was thrown down, which was treated in the same manner as described for the soluble part of the mineral. Mercury was again present in traces, as well as substances which came down in place of bismuth and cadmium; these were probably identical in nature with those found in the other portion. After the supposed cadmium had been filtered off, the solution was evaporated and heated; a residue was left (ρ). The ammonia group consisted only of aluminium, iron, and uranium. To the filtrate from this group ammonium carbonate was added; no precipitate came down, until after twenty-four hours, when a white substance separated. The filtrate left no residue after it had been evaporated and heated.

The precipitate mentioned above, which was obtained by adding hydrochloric acid to the solution of the fused mass, was once more fused with bisulphate, and dissolved in hot water (solution γ); a residue remained, which was partly soluble in concentrated hydrochloric acid (solution α), and a white residue was left. Sulphuretted hydrogen was then passed through solution α , and after twenty-four hours standing, a brownish red precipitate was formed, the filtrate from which was mixed with solution β , obtained in the following way:—The solution γ had become turbid, and deposited a white precipitate; this was removed by filtration. Sulphuretted hydrogen was passed through the filtrate, and gave a precipitate similar in appearance to that formed in solution α ; after filtering and allowing to stand, saturated with sulphuretted hydrogen for twenty-four hours, another quantity of what was apparently the same substance was obtained. The mixed solutions α and β were then oxidised, precipitated with ammonium hydroxide, and the precipitate dissolved in dilute hydrochloric acid. No precipitate was produced with ammonium oxalate, but only a slight turbidity, which passed away on addition of a few more drops. The oxalic acid was removed from this solution by evaporation and ignition, and the oxide was weighed. Qualitative tests showed that it consisted of oxide of titanium with traces of oxide of zirconium.

A separate quantity of the mineral was heated to redness, in order to determine the loss on ignition. It proved to be considerable, and chiefly due to the presence of water. The gas evolved was collected over mercury, and the carbon dioxide absorbed with caustic potash; the only other gas present was helium. From 1 grm. of the mineral 8.2 c.c. of helium were obtained at normal temperature and pressure.

The results of the analysis are given in Table II., where the measurements of radio-activity of the various precipitates are also given, contrasted with that of the mineral taken as 100.

For determining the radio-activity of the precipitates, a month was allowed to elapse after they had been obtained; about 10 m.grms. of the substance, if as much was available, was weighed out and placed in an electroscope. It was sometimes necessary, however, to place precipitate

and filter together in the electroscope. The time in which the leaf moved over 20 divisions of the scale was noted, and from this the number of divisions per hour was calculated, allowance having been made for one hour's leakage, had exactly 10 m.grms. been placed on the copper plate. The figures thus obtained are given in the third column of the table, and in the second column the activity of the total quantity of the precipitate, obtained by multiplying the numbers in the third column by the weight of the substance, is recorded. The last column shows the percentage activity, that of the original mineral being taken as 100.

The mineral possesses 83.3 per cent of the activity of standard uranium oxide, a sample several years old. It is also to be noticed that the activity is associated almost entirely with the soluble part of the mineral; while the ratio of the weights of the soluble to the insoluble portion is 40 to 1, the ratio of the activities is about 300 to 1. Again, comparing the activity of constituents common both to the insoluble and soluble portions, such as iron oxide, and bismuth (?) oxide, the samples from the soluble portion are much more active than those of the insoluble portion. In the case of iron the ratio is 17 to 1.

Nearly all the precipitates obtained from the soluble portion proved to be radio-active, although some had only a very slight effect on the electroscope. A remarkable exception is furnished by the alumina, which, although closely allied to the strongly active iron group, is absolutely inactive. The active constituent of the iron group is therefore insoluble in excess of caustic potash; as further experiments showed, it gives off an emanation, the rate of decay of which, although not accurately determined, appears to point to its being due to that of radiothorium, separated by Hahn, which always comes down with iron ("Jahrb. f. Radioaktivität," 1905, vol. ii.).

The activity of several precipitates had not reached a maximum at the last measurement; those of lead, iron, uranium, cerium, and calcium were still increasing, while the activity of bismuth (?), thorium, and zirconium did not change. On the other hand, several precipitates showed activity originally, which decreased and even disappeared, e.g., ω , insoluble in hydrochloric acid* (see above). When originally obtained, it was placed in the electroscope along with its filter, and showed an activity of 30,000 to 40,000. After destroying the filter, and dissolving the precipitate with aqua regia, and evaporating the solution to dryness, the activity had decreased to 250, and it seemed then to be permanent at that value. It may be assumed, therefore, that this precipitate is a so-called X-substance; its chemical behaviour somewhat resembles that of a platinum metal. After evaporation, the solution in aqua regia left a yellow crystalline residue, which turned black when gently heated. This black residue was insoluble in hydrochloric acid, but soluble in aqua regia; the solution showed again the same properties.

The next most active precipitate was found in the filtrate from the ammonia group. Several very active minute traces of substance were collected on filters. The substance ϕ , mentioned above, obtained by addition of sodium phosphate, weighed only 8 m.grms., and had a total activity of 3400, which increased to 3900 after standing for six weeks. Although this precipitate forms only 0.02 per cent of the total weight of the mineral, it possesses 1 per cent of the total activity. In connection with this it may be remembered that Rutherford (*Chem. Soc. Trans.*, vol. lxxxi., p. 345) during his early experiments on thorium and thorium-X, also found a strongly active constituent in his thoria, precipitable by sodium phosphate after removal of the thoria. He was not always able to detect it, however, and ascribed it to the presence of an impurity in commercial thoria.

In conclusion, it is my pleasant duty to express my hearty thanks to Sir William Ramsay for his kind assistance and advice.

* The residue, ρ , was also initially very active, but lost its activity in a short time.

A REVISION OF THE ATOMIC WEIGHT OF
CADMIUM.*By GREGORY PAUL BAXTER, MURRAY ARNOLD HINES,
and HARRY LOUIS FREVERT.

(Continued from p. 235).

Method of Analysis (continued).

From the corrected weight of the cadmium bromide very nearly the requisite quantity of pure silver was calculated. This silver was weighed out and dissolved, in a flask provided with a column of bulbs to prevent loss of silver by splattering, in re-distilled nitric acid diluted with an equal volume of water. After the silver was dissolved, the solution was diluted to twice its volume, and was heated until free from nitrous fumes. Then it was still further diluted until not stronger than 1 per cent, and was slowly added, with constant stirring, to the 1 per cent solution of cadmium bromide in the precipitating flask. In three analyses (4, 5, and 8), this procedure was varied by adding the bromide to the silver nitrate. After being shaken for some time, the solution was allowed to stand several days, with occasional shaking, until the supernatant liquid was clear. Thirty c.c. portions of the solution were then tested with hundredth normal solutions of silver nitrate and sodium bromide in the nephelometer (Richards and Wells, *Am. Chem. Journ.*, 1904, xxxi., 235) for excess of bromide of silver, and, if necessary, either standard silver nitrate or sodium bromide solution was added, and the process of shaking and testing repeated, until the amounts of bromide and silver in the solution were equivalent. If the solution was perfectly clear when tested, and contained no considerable excess of bromide or silver, the test solutions were discarded, since they contained only negligible amounts of dissolved silver bromide; otherwise they were returned to the flask and a correction was applied for the silver bromide thus introduced.

As soon as the exact end-point of the titration had been found, about 4 centigrams of silver nitrate in excess were added, to precipitate dissolved silver bromide, and the flask was again shaken and allowed to stand until clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible, after it had been washed by decantation about eight times with pure water. Then it was heated in an electric air-bath, first for several hours at 140°, finally for an hour at 200°, and, after it had cooled in a desiccator, it was weighed. In order to determine how much moisture was retained by the precipitate, in each case it was transferred as completely as possible to a clean porcelain crucible and weighed; then the salt was fused by heating the small covered crucible, contained in a large crucible, and again weighed. After fusion the silver bromide was light yellow, with only a trace of darkening, showing that no appreciable reduction had taken place. The asbestos mechanically detached from the Gooch crucible, together with a minute quantity of silver bromide which occasionally escaped the crucible, were collected from the filtrate and wash-waters upon a small filter, the ash of which was treated with nitric and hydrobromic acids before weighing. Although the filtrates and first wash-waters were essentially free from dissolved silver bromide, the subsequent wash-waters usually contained a trace of this substance. The amount of dissolved salt was determined with the nephelometer by comparison with standard bromide solutions. Finally, the weight of silver bromide was corrected for the sodium bromide introduced.

Although in our analyses of cadmium chloride no evidence could be obtained of appreciable occlusion of either cadmium or silver salts by silver chloride, especial precautions were taken to avoid any possibility of such a difficulty in this research. In the first place both the cadmium bromide and the silver nitrate solutions were extremely dilute during precipitation, each one having a

volume of about 1 litre. In the second place the method of precipitation was varied by sometimes adding the silver nitrate to the cadmium bromide (Analyses 1, 2, 3, 6, and 7), and sometimes adding the bromide to the silver (Analyses 4, 5, and 8). And in the third place the solutions were allowed to stand varying lengths of time before the titration was completed, so that occluded substances might have opportunity to be dissolved. Analysis 1, in which the largest quantity of bromide was employed, over 11 grms., which is to be expected to give the most marked evidence of occlusion, was not tested for five days after precipitation, and the titration was completed eight days later. In the other analyses the period between precipitation and the completion of the titration varied from seven days in Analysis 4 to three days in Analysis 8. Furthermore, in some cases, after the end-point had been reached, the solutions were allowed to stand some days longer with occasional testing. No change in end-point with standing was observed. In spite of these differences in the method of procedure, the variations in the final results do not exceed the experimental error to be expected, except in the case of Analyses 4 and 12. Evidently, occlusion of any sort must have been very slight if it existed at all. Analyses 4 and 12, performed with the same bromide, differ so markedly from the others that, although no reason for the difference is known, they are rejected in computing the final average.

The gold-plated brass weights were carefully standardised to hundredths of a milligram. Vacuum corrections of +0.000090 for cadmium bromide, of +0.000046 for silver bromide, and of -0.000031 for silver were applied. (The specific gravity of cadmium bromide has recently been found to be 5.192; Baxter and Hines, *Am. Chem. Journ.* 1904, xxxi., 220). All weighings were made by substitution with counterpoises as nearly like the objects to be weighed as possible. The atomic weight of silver is assumed to be 107.930 and that of bromine to be 79.955.

The analytical work was performed wholly by Mr. Hines.

The ratios of silver used to silver bromide obtained in the same analyses afford sufficient proof of the purity of the bromine and silver, as well as confirmatory evidence of the absence of appreciable occlusion by the silver bromide.

		Ag:AgBr.	
Analyses 1 and 9		57.4444	
" 2 "	10	57.4464	
" 3 "	11	57.4436	
" 4 "	12	57.4436	
" 5 "	13	57.4421	
" 6 "	14	57.4438	
" 7 "	15	57.4428	
" 8 "	16	57.4429	
Average		57.4437	

The most probable value for this ratio has been shown both by Stas and by experimenters in this laboratory to be 57.4445 (Richards, *Proc. Am. Phil. Soc.*, xliii., 119).

In recent experiments in fusing manganous chloride, in a current of hydrochloric acid gas which had been dried by concentrated sulphuric acid and finally by means of phosphorus pentoxide, an insoluble residue of manganous phosphate was invariably obtained when the salt was dissolved in water. The quantity of this residue varied with the amount of moisture contained by the salt when brought in contact with the hydrochloric acid gas, being extremely slight if the salt was very nearly dry, but amounting to several m.grms. if the salt still contained much of its crystal water. Although it seemed certain that the phosphorus had its origin in the phosphorus pentoxide, and was volatilised in the form of either phosphorus pentachloride or oxychloride through the action of the hydrochloric acid upon the pentoxide, in order to obtain still more positive evidence that this was really the case, the experiment was tried of passing hydrochloric acid gas which had been dried

* From the *Journal of the American Chemical Society*, xxviii., No. 6.

THE ATOMIC WEIGHT OF CADMIUM.

(Ag = 107.930. Br = 79.955.)

Series I. CdBr ₂ : 2Ag.	No. of analysis.	Sample of CdBr ₂ .	Weight of CdBr ₂ in vacuum (grms.).	Weight of resi- due (grm.).	Loss in weight of boat (grm.).	Weight of Ag in vacuum (grms.).	Weight of Ag added or sub- tracted (grm.).	Corrected wt. of CdBr ₂ (grms.).	Corrected weight of Ag (grms.).	Atomic weight of cadmium.
	1.	II.a	11.46220	0.00008	0.00004	9.08409	-0.00030	11.46216	9.08379	112.468
	2.	II.b	6.82294	0.00018	0.00006	5.40734	-0.00010	6.82282	5.40724	112.461
	3.	II.a	6.75435	0.00011	+0.00004	5.35297	-0.00020	6.75420	5.35277	112.465
	4.	III.a	7.08590	0.00006	0.00004	5.61567	+0.00030	7.08588	5.61597	112.449
	5.	III.a	5.13867	0.00008	0.00000	4.07236	-0.00010	5.13859	4.07226	112.473
	6.	III.a	5.84328	0.00008	0.00004	4.63092	-0.00020	5.84324	4.63072	112.471
	7.	III.a	5.99712	0.00008	0.00000	4.75269	-0.00010	5.99704	4.75259	112.472
	8.	II.a	5.90811	0.00017	0.00002	4.68200	0.00000	5.90796	4.68200	112.472

Average, rejecting Analysis 4 112.470

Series II. CdBr ₂ : 2AgBr.	No. of analysis.	Sample of CdBr ₂ .	Weight of CdBr ₂ in vacuum (grms.).	Weight of resi- due (grm.).	Loss in weight of boat (grm.).	Weight of AgBr in vacuum (grms.).	Loss on fusion (grm.).	Weight of as- bestos from filtrate (grm.).	Weight of AgBr from wash- waters (grm.).	Corrected wt. of CdBr ₂ (grms.).	Corrected wt. of AgBr (grms.).	Atomic weight of cadmium.
	9.	II.a	11.46220	0.00008	0.00004	15.81286	0.00024	0.00024	0.00033	11.46216	15.81319	112.466
	10.	II.b	6.82294	0.00018	0.00006	9.41251	0.00028	0.00044	0.00000	6.82282	9.41267	112.469
	11.	II.a	6.75435	0.00011	+0.00004	9.31815	0.00028	0.00043	0.00000	6.75420	9.31830	112.460
	12.	III.a	7.08590	0.00006	0.00004	9.77557	0.00013	0.00053	0.00052	7.08588	9.77649	112.444
	13.	III.a	5.13867	0.00008	0.00000	7.08897	0.00007	0.00043	0.00000	5.13859	7.08933	112.461
	14.	III.a	5.84328	0.00008	0.00004	8.06076	0.00005	0.00033	0.00026	5.84324	8.06130	112.467
	15.	III.a	5.99712	0.00008	0.00000	8.27321	0.00012	0.00020	0.00031	5.99704	8.27360	112.463
	16.	II.a	5.90811	0.00017	0.00002	8.15022	0.00015	0.00037	0.00026	5.90796	8.15070	112.463

Average, rejecting Analysis 12 112.464

Average of Series I. and II. 112.467

thoroughly by means of sulphuric acid, first over phosphorus pentoxide which had been freshly sublimed in a current of dry air, and then into water. The aqueous solution, upon evaporation and testing with ammonium molybdate gave a considerable amount of the characteristic ammonium phosphomolybdate. This result confirms that of Bailey and Fowler (CHEMICAL NEWS, LVIII., 22), who have found that both hydrochloric and hydrobromic acids react with phosphorus pentoxide at ordinary temperatures to form the oxychloride and bromide of phosphorus respectively. The manganous phosphate, then, must have been produced by the action of the volatilised chloride of phosphorus upon the moisture contained by the manganous chloride to form phosphoric acid, and subsequent displacement of hydrochloric acid from the salt by the phosphoric acid.

Although in our previous work with cadmium chloride, where the double cadmium ammonium chloride, CdCl₂NH₄Cl, was fused in a current of hydrochloric acid gas which had been finally dried with phosphorus pentoxide, the salt, which contains no crystal water, was essentially free from moisture before coming in contact with the hydrochloric acid, yet it seemed desirable to repeat the experiments with cadmium chloride in such a way that the danger mentioned above could be completely avoided. This result was easily attained by drying the hydrochloric acid gas with concentrated sulphuric acid only, four columns about 30 c.m. in length, filled with beads moistened with sulphuric acid, being used for the purpose.

In order to ascertain whether concentrated sulphuric acid is appreciably attacked by hydrochloric acid gas, a large quantity of this gas was conducted through the columns and then into water. The aqueous solution was then evaporated and tested for sulphate with barium

chloride. Although a slight precipitate of baric sulphate was produced, the quantity was estimated by comparison in a nephelometer with a standard solution of a sulphate to be less than five-hundredths of a milligram. Evidently nothing is to be feared from this source.

The material for these experiments was prepared from a portion of Fraction II. of cadmium sulphide by first depositing the metal electrolytically from the sulphate, as previously described, and then dissolving the washed cadmium in pure hydrochloric acid in a platinum dish. The chloride does not lend itself readily to crystallisation from aqueous solution, on account of its great solubility even at low temperatures, but by conducting hydrochloric acid gas into the solution the much less soluble double salt with hydrochloric acid, CdCl₂.2HCl.7H₂O, was formed. The salt was thus crystallised three times with centrifugal drainage, to free it from the trace of sulphates occluded by the metal during electrolysis. Finally, it was dried and freed from hydrochloric acid as far as possible in a vacuum desiccator containing solid potassium hydroxide.

In Analysis 18 the same specimen of silver was used as in Analyses 4 to 8. In Analyses 17 and 19 a new specimen, which had been twice electrolysed, was employed.

The fusion, bottling, and analysis of the salt were conducted exactly as described in the previous paper on cadmium chloride, and also in this paper. A very slight insoluble residue in the cadmium chloride was determined as in the case of the bromide. The vacuum correction, +0.000156, was applied to every apparent grm. of cadmium chloride, and of +0.000075 for every apparent grm. of silver chloride. (The specific gravity of cadmium chloride has already been found to be 4.047; Baxter and Hines, *Am. Chem. Journ.*, 1904, xxxi., 220). The analytical work was performed by Mr. Hines.

(To be continued).

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, November 1st, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society through the death, on October 19th. of Geh. Rath Professor Fedor Beilstein, who was elected an Honorary and Foreign Member on February 1st, 1883.

Messrs. H. R. Cooper, F. E. E. Lamplough, and W. H. Rawles were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Richard Abegg, Ph.D., Landberstrasse 4, Breslau, Germany; William Heath Bayliss, Brewery House, Ashwell, Herts; Charles George Edgar Farmer, 16, Herbert Crescent, S.W.; David Paton Grubb, B.Sc., Windsor Hill, Newry; John Hamer, 44, Sugden Road, Clapham Common, S.W.; Alexander Edmund Middleton, 112, South Park Road, Wimbledon, S.W.; Arthur Higgs Morris, 77, Beverly Road, Bolton, Lancs.; Arthur Percival Newton, B.Sc., Red Cot, Coulsdon, Surrey; Benjamin Dawson Porritt, 33, South Park Hill, South Croydon; Herbert Stanley Redgrove, 137-140, Tottenham Court Road, W.; William R. R. Starling, 23, Magdalen Road, Norwich.

Of the following papers, those marked * were read:—

*190. "*A Development of the Atomic Theory which Correlates Chemical and Crystalline Structure and Leads to a Demonstration of the Nature of Valency.*" By WILLIAM BARLOW and WILLIAM JACKSON POPE.

The authors represent atoms in the combined state by "spheres of influence," and inquire how such spheres can be close-packed in a homogeneously symmetrical manner so as accurately to simulate crystalline compounds. An examination of the geometrical properties of close-packed assemblages of spheres shows that the atoms of the elements must be represented by spheres of influence directly proportional in volume to their fundamental valencies, and that a close-packed assemblage built up of spheres of the appropriate sizes, so as to represent some particular compound, can be partitioned into units identical with the chemical molecule, and possesses symmetry and dimensions compatible with those of the crystalline substance.

A detailed inquiry concerning benzene, triphenylmethane, naphthalene, anthracene, and their derivatives, shows that, with the inclusion of the above assumption, all the requisite data are available for precisely determining the configuration of the benzene molecule. The configuration deduced is in accordance with the crystallographic and chemical evidence, and leads to an explanation of the meta-, ortho-, para-law of substitution, and of other previously unexplained features of the chemistry of aromatic substances.

In addition to the geometrical property, which demonstrates that valency is a volume relation, it is shown that close-packed homogeneous assemblages of spheres possess others which lead to simple physical interpretations of multivalency and tautomerism. It is also indicated that ethylenic and acetylenic bonds and isomerism have complete analogues in peculiarities of homogeneous assemblages of spheres.

The relations briefly indicated above have been worked out in detail, and are shown to be in entire agreement with the quantitative evidence afforded by the crystallographic measurements of the compounds concerned.

DISCUSSION.

Prof. ARMSTRONG, after expressing his opinion that the communication was one of altogether fundamental importance, in the first place referred to it as showing the extreme value to chemists of the study of crystallography—

a subject of which hitherto relatively far too little notice had been taken. It was to be hoped that a sense of proportion would begin to prevail, and that the study of form would now receive proper attention. The success with which the authors appeared to have correlated crystalline form with structure was very remarkable, especially their determination of the manner in which water or other complexes became attached in one particular direction to a molecule—slabwise. Perhaps the most important feature of the communication and the most interesting to chemists, at present, was the manner in which valency was accounted for as a volume property, and a very ingenious explanation given of varying valency. In particular, he had been struck, when discussing the work with Professor Pope, by the explanation which was given of the departure from the ordinary law of increase or decrease of valency by two units at a time (the law of odd or even valency) observed in the case of the simpler compounds of an element—as in the oxides of nitrogen, for example. Hitherto, chemists had been forced to deal with variation of valency simply as a fact; they were now, for the first time, presented with an explanation of the cause of variation and of the manner in which this was effected.

Another point of extreme interest was the view put forward that it could not be supposed that elements preserved a constant "atomic volume," since it was often found, in cases in which the introduction of a radicle involved an alteration in volume, that the complex changed as a whole, the original form being preserved, alteration taking place proportionally along each axis.

Like the theory of structure at present in use, the mode of treatment now advocated did not enable us to deal with the dynamical side of chemical phenomena; it was to be regarded as an amplification of that theory, not as overriding it or as proving it to be in any way inconsequent. The opportunities it afforded of discussing problems which had eluded our grasp hitherto appeared to be very numerous.

Mr. JOHN CASTELL-EVANS asked whether he had rightly understood Professor Pope's statement relative to the substitution of two or more spheres for one? As he understood it, Professor Pope seemed to say "that if from a closely packed aggregation of spheres one individual sphere of volume m be removed, the resulting cavity could be filled by m spheres each of unit volume and the 'close packing' be still preserved." This is not the case; if a cube, say, be described about the sphere of volume m , then into this cube m unit spheres could be packed, but certainly not into the cavity left by the removal of the original sphere.

Mr. BALY pointed out that the particular assemblage of atoms adopted by Professor Pope for the benzene molecule would only exist in the benzene crystal. In the liquid state the molecule of benzene would probably not exist in the rigid condition pictured by the authors; there would seem to be no doubt that the molecule possesses an inherent tendency to vibrate, this tendency being dependent very largely on the temperature. Probably the melting-point of a crystal marks the temperature at which the tendency to vibrate on the part of the molecules overcomes the elastic energy of the crystalline form. Inasmuch as the reactions of benzene and its compounds usually take place with the substance in solution or in the liquid state, any property based only on the rigid structure in the crystal would not necessarily hold good. For example, the authors base an explanation of the ortho-, meta-, and para-substitution on this rigid structure. Owing to the dynamic condition obtaining during reactions this explanation would seem to fall to the ground.

Mr. WOOLHOUSE expressed surprise that in the complex NaNO_3 the element C with a volume of 4 could replace the N with a volume of 3, and that the element Ca with a volume of 2 could replace the Na with a volume of 1, and yet calcite could have such a similarity of crystalline form, as it is known to have, to that of sodium nitrate.

Although the replacement of N by C might leave the

x, y, z ratios the same in spite of the increase of each, still the substitution of Ca for Na must result in an alteration of shape of the complex, resulting in the increase of at least one of these values.

Prof. MIERS, speaking as a crystallographer, stated his conviction that the new theory propounded by the authors was destined to be of immense value in the problems of crystal structure.

Crystallographers were accustomed to treat these as static problems, and (largely owing to the researches of Mr. Barlow) feel fairly confident that they now know something of the manner in which the crystalline material is arranged. The principle of packing was liable to suspicion so long as there was no clue to the nature of the units, but had now acquired quite a new meaning with the valency volumes to indicate the dimensions of the bodies to be packed: so that we might now hope to realise a true model of the crystal structure.

The case of the Humite group, in which the increase of an axis is absolutely proportional to the valency volume of the introduced radicle, was in his opinion a very convincing one. The theory was one of profound interest to all students of crystals.

Dr. TUTTON said that he considered a notable advance had been made by the authors of this paper, which furnished another example of the advantages of the study of crystallography by chemists, an object which he had long been striving to further. There appeared to be three salient points in the work, the results of which were laid before the Society that evening. The first was the emphasis of the individual influence of the atom as distinguished from the properties of the molecule as a whole, and the influence of certain predominating atoms in particular in determining those properties. This had been one of the chief results of his (Dr. Tutton's) own work on the sulphates and selenates, and the present work was based on that now absolutely incontrovertible foundation. The second point was that the teaching of the "topic axial ratios," introduced to the Society by him (Dr. Tutton) in the year 1894, simultaneously with and independently of Dr. Muthmann in the *Zeitschrift für Kristallographie*, was now advanced by the authors of the present paper a step further, inasmuch as in the formulæ for those ratios the term V respecting the molecular volume would now be replaced by W , the valency volume. Not only did this involve the remarkable geometrical explanation of valency which had been explained to them, but, and this was the third point which the speaker desired to emphasise, it enabled the ratios in question to be no longer confined to exhibiting in a highly instructive manner the structural relationships between the members of the same series of isomorphous compounds, but connected various series together, and indeed, in general, enabled comparisons to be made between compounds of totally dissimilar, as well as of similar, nature. It was therefore obvious that a great advance in the correlation of chemical composition and crystalline form had been made.

Mr. W. BARLOW pointed out that the spheres employed to picture the equilibrium conditions of the atoms must not be regarded as actually existent in nature; the actual spheres of influence of the atoms are not supposed to be separated by interstices, and the models are merely the best means that the authors have found for expressing, in a concrete form, the results of their researches. The balls used to represent the atomic spheres of influence should be made of solid soft indiarubber, so as to be elastic and deformable, but not compressible, and the close-packed assemblages, composed of balls of appropriate sizes, should be compressed to an extent which will practically annul the interstices.

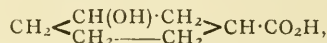
Prof. POPE said that in the substitution referred to by Mr. Evans, the interstitial space is regarded as available for occupation by the new contents of the cavity. The total space available for the substituting spheres is thus not spherical, but of the irregular shape bounded by the curved surfaces of the enveloping spheres.

The series of substitutions as a result of which the NaNO_3 assemblage is converted into that of CaCO_3 can be performed so that the crystalline form changes but slightly, although the equivalent parameters x, y , and z increase, but remain equal to one another in accordance with the rhombohedral symmetry.

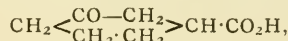
It is not claimed that the rigid assemblage of solid spheres represents accurately the condition of crystalline benzene; the spheres of atomic influence may well be regarded as domains of considerable dynamic activity. The existence of "liquid crystals" suggests that much symmetry of arrangement occurs transiently in liquids generally, and the uniformity of chemical reaction in solution must be largely attributable to symmetry of arrangement as between reacting molecules. There is no reason to suppose that considerable change in molecular configuration attends the liquefaction of benzene; as the suggested mode of regarding the meta- and ortho-para-law only postulates symmetry of arrangement, it appears to be perfectly valid.

191. "Synthesis of Carvestrene." (Preliminary Notice). By WILLIAM HENRY PERKIN, jun., and GEORGE TATTERSALL.

When *m*-hydroxybenzoic acid is reduced by means of alcohol and sodium, it is converted into hexahydro-*m*-hydroxybenzoic acid,—

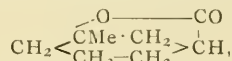


which crystallises from ether, and melts at $130\text{—}132^\circ$ (compare Einhorn, *Annalen*, 1896, ccxc., 298). Oxidation with potassium bichromate and sulphuric acid converts this hydroxy-acid into γ -ketohexahydrobenzoic acid,—

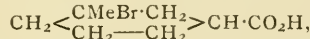


which had previously been obtained only in the form of a syrup (Baeyer and Tutein, *Ber.*, 1889, xxii., 2182; Einhorn, *loc. cit.*, p. 304; Goodwin and Perkin, *Trans.*, 1905, lxxvii., 852). It crystallises from benzene in glistening prisms, melts at $75\text{—}76^\circ$, distils as 210° (25 m.m.), and yields a semicarbazone melting at $182\text{—}183^\circ$ with decomposition.

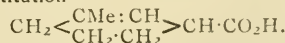
Ethyl γ -ketohexahydrobenzoate (b. p. 150° under 30 m.m.) reacts with magnesium methyl iodide with the formation of the lactone of γ -hydroxyhexahydro-*m*-toluic acid,—



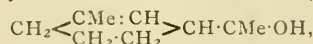
a colourless oil which distils at 145° (20 m.m.), and when heated with hydrobromic acid is quantitatively converted into γ -bromohexahydro-*m*-toluic acid,—



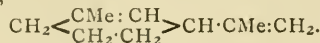
which, so far, has only been obtained in the form of a syrup. It readily loses hydrogen bromide when treated with pyridine, and is converted into a tetrahydro-*m*-toluic acid of boiling-point $142\text{—}144^\circ$ (15 m.m.), which probably has the constitution—



The ester of this acid (b. p. 128° under 60 m.m.) reacts readily with magnesium methyl iodide, and is almost quantitatively converted into Δ^1 -*m*-menthenol (8),—



which had not previously been prepared. This tertiary alcohol distils at $110\text{—}112^\circ$ (30 m.m.), has a pleasant odour of menthol and terpineol, and when digested with potassium hydrogen sulphate is almost quantitatively decomposed with elimination of water and formation of carvestrene,—



The hydrocarbon thus obtained distilled at 179–180°, and yielded a *dihydrochloride*, $C_{10}H_{16}, 2HCl$, melting at 52.5°, and a *dihydrobromide*, $C_{10}H_{16}, 2HBr$, melting at 48°. Its solution in acetic anhydride was coloured deep blue by the addition of sulphuric acid.

Since these properties coincide exactly with those of carvestrene, which Baeyer (*Ber.*, 1894, xxvii., 3488) first prepared by the distillation of vestrylamine hydrochloride, and which Baeyer and Villiger (*Ber.*, 1898, xxxi., 1402) subsequently proved to belong to the *m*-cymene series, there can be little doubt that the above experiments are to be regarded as a synthesis of this important terpene.

(To be continued).

NOTICES OF BOOKS.

Report on the Advancements of Pharmaceutical Chemistry and Therapeutics. Vol. XIX. Darmstadt: E. Merck. 1906.

THESE Reports on the Advancements of Pharmaceutical Chemistry and Therapeutics are sent gratis to medical men and others interested in pharmacology on application to 16, Jewry Street, E.C. Although the compiler has an interest in the manufacture of many of the preparations which he discusses at length, the report is sufficiently impartial to be worthy of attention as a work of reference, and no new preparation is overlooked if it appears to be really valuable. Moreover, information is given, with copious references to original papers, regarding fresh uses of well-known drugs, besides full details of cases which have exhibited specially interesting features.

Petroleum and its Products. By Sir BOVERTON REDWOOD, D.Sc., &c. Second Edition. London: Charles Griffin and Co., Ltd. 1906.

THE new edition of this standard work is in every respect an admirable treatise on the occurrence, properties, production, and uses of petroleum, and nobody who takes a scientific or practical interest in any of the numerous branches of the great industry can afford to be without a copy. The work now occupies two volumes, for although it has been found possible to condense some portions, the advance of knowledge has necessitated considerable additions to various chapters. Many new maps and figures are included, and, moreover, a complete bibliography has been added; the preparation of this last section, which occupies nearly a quarter of Volume II., must have been a formidable piece of work, but it will undoubtedly be greatly appreciated. The author has had the advantage of valuable assistance from some of the most eminent authorities on the geological and geographical distribution of petroleum and natural gas, and on the practical methods of the production and refining of petroleum, and he has brought his treatise to such a state of excellence as to enable it to compare favourably with most works in any language.

Nitro-Explosives. By P. GERALD SANFORD, F.I.C., F.C.S. Second Edition. London: Crosby Lockwood and Son. 1906.

IN the second edition of a treatise on a rapidly growing branch of science the reader expects to find full information relative to its most recent developments, and in this case he will not be disappointed, for the revision of the first edition has been very thoroughly performed. The chapter on smokeless powder, for instance, has been greatly enlarged, and many details of composition and manufacture are now included which did not find a place in the earlier edition. A critical examination of the book for deficiencies regarding modern processes and practice has brought to light only one omission which can be re-

garded as of importance, and this relates to the freezing-point determinations of nitro-glycerin. Nauckhoff's work on the subject is abstracted and reviewed, but no mention is made of recent research on dinitro-glycerin, which seems to be a suitable substance for dissolving in nitro-glycerin to lower the freezing-point, and for the manufacture of which Mikolajczak not long ago patented a process. The features of the book, which did so much to recommend the earlier edition, namely, the systematic arrangement and the thoroughly practical treatment of all nitrated substances, are still conspicuous in the second edition, which is a valuable contribution to the literature of nitro-explosives.

General Principles of Organic Syntheses. By P. ALEXEYEFF. Authorised Translation by J. MERRITT MATTHEWS, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1906.

THIS volume is based upon a monograph which was published as long ago as 1899 by the late Professor Alexeyeff, of the University of Kieff. The translator has worked in much new material, and has made extensive alterations, so that the English edition is more than a mere translation of the Russian original. It will be found most useful in co-ordinating the knowledge of the advanced student who has already some acquaintance with the elements of organic chemistry, and with its help he cannot fail to widen his views and strengthen his grasp of a subject which sometimes appears to present a bewildering mass of unorganised details. The plan of the book is to group together general methods employed in organic chemistry—such as oxidation, reduction, fixation and removal of radicals, condensations, &c.—and to consider them from a theoretical point of view, generalising and explaining the choice of various reagents for different purposes. No practical details relating to the apparatus, &c., to be employed are given, for the book is intended, not to replace, but to supplement a laboratory manual; it deserves to be well received by teachers and advanced students, and those engaged in research work will gather useful information from it.

Technologie der Fette und Ole. ("Technology of Fats and Oils") By GUSTAV HEFTER. Vol. I. Berlin: Julius Springer. 1906.

THE author of this treatise has observed that, while the last two decades have seen the publication of several works on the analysis of fats, no book devoted exclusively to the technology of the fat industry has appeared, although monographs on various branches have been issued. To supply this want of a comprehensive modern work on the oil and fat industries has been his special aim. The occurrence, constituents, and properties of the natural oils, fats, and waxes are treated comparatively briefly, while the general methods of extraction are discussed more fully; different processes and apparatus are described with copious illustrations and plans. Although, naturally, special prominence is given to German practice, English, American, and French methods all find a place in the book, which will be the more useful, both in Germany and other countries, on account of this cosmopolitan policy. The by-products of the industries are fully treated, as regards both properties and utilisation; for instance, the manufacture of oil cakes is discussed, data concerning their average composition, price, &c., being given. The whole is very carefully indexed, and will be a valuable addition to the library of the manufacturer and chemist.

Cours de Chimie Organique. ("Course of Organic Chemistry"). By FRÉD. SWARTS. Paris: A. Hermann. 1906.

IN this book the course of lectures on organic chemistry delivered by the author at the University of Gand is reproduced, with somewhat fuller treatment of parts of the subject, of which time did not allow an extended discussion

in the lectures. The book is occupied more with descriptive and theoretical organic chemistry than with practical work, and the theory of the science is particularly well treated. The author goes systematically through the most important classes of fatty and aromatic compounds, thus providing a very good elementary course, although there appear to be no special novelties of treatment to notice. Some technical processes are introduced, and attention is paid to industrial applications, while general methods of preparation are specially emphasised. A useful feature is the introduction of theoretical discussions at convenient points in the text, which should help the beginner to obtain a good grasp of the theory of organic chemistry, the logical method of first discussing facts and then basing theories upon them being far the most successful way of presenting the subject.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 17, October 22, 1906.

Existence of Bromine Chloride.—Paul Lebeau.—The author's investigations lead him to the conclusion that the compound hitherto known as bromine chloride does not exist, the constant composition of the mixture being due to the circumstances of its formation. In fact, it corresponds to the solubility of chlorine in bromine at the temperature of 0°. No other combinations take place by the direct action of chlorine on bromine. The crystals which are obtained by sufficiently cooling a solution of bromine in liquid chlorine have a composition depending on their temperature of formation, and they are proved to be merely mixed crystals of chlorine and bromine.

Cæsium Protoxide.—E. Rengade.—It is possible to prepare well-defined cæsium protoxide in a perfectly pure crystalline condition by evaporating a solution of the oxide in an excess of cæsium. It is thus obtained in the form of orange-red crystals, which react violently on water and decompose at about 500° when in contact with silver and in the cold when in contact with liquefied ammonia. In the latter case, the protoxide is transformed into a mixture of amide and hydrate of cæsium. The formula of the protoxide is found by estimating the cæsium and measuring the oxygen used in the experiment (Cs_2O). The author is also preparing, by the same method, the oxides of rubidium and potassium.

Pure Alloys of Manganese and Tungsten, and Preparation of Tungsten Metal.—G. Arrivant.—By the action of powdered aluminium on a mixture of the oxides of the metals it is possible to obtain alloys of tungsten and manganese rich in tungsten, but their separation is often incomplete, and the author devises a better method. To obtain alloys rich in manganese, he heats a mixture of the powdered metals in a current of hydrogen in a Schlesing furnace. However, no alloy containing more than 25 per cent of tungsten can be prepared by this method. By reducing suitably selected mixtures of oxides of manganese and tungsten by means of aluminium, the author prepares alloys containing up to 60 per cent of tungsten. These bodies do not appear to contain the metals in a combined state, and when treated with dilute acids they leave a residue of pure tungsten, which method can be used as a means of preparing the metal.

Condensation Products of Acetylenic Ethers with Amines.—Ch. Moureu and I. Lazennec.—The products of condensation of the acetylenic ether salts, $\text{R}-\text{C}\equiv\text{C}-\text{CO}_2\text{R}'$, with amines are non-basic bodies,

which can easily be hydrolysed by acids; the hydrolysis causing the amine to form again in addition to the β -ketonic ether, $\text{R}-\text{CO}-\text{CH}_2-\text{CO}_2\text{R}'$. This reaction constitutes a new and excellent method of transforming acetylenic ethers into β -ketonic ethers.

Atomic Weight of Dysprosium.—G. Urbain and M. Dementitroux.—The mean of a number of experiments gives the atomic weight of dysprosium as 162.54, the method used being the transformation of the hydrated sulphate of formula $\text{Dy}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$ into the oxide, Dy_2O_3 .

Presence of Formol in various Foods.—G. Perrier.—The author investigates the proportion of the minute traces of formol in various food materials.

Azoic Dyes: Their Heat of Combustion and Formula of Constitution.—P. Lemoult.—The author finds the heat of formation of a large number of azoic dyes. He finds that, in their actual state, the azoic dyes can be represented with great exactitude as azo-carbides on which are fixed the OH or NH_2 groups. Perhaps also, under certain circumstances, quinonisation takes place, but the author is further investigating this latter question.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 12, 1906.

Atomic Weight of Tantalum.—F. Willy Hinrichsen and N. Sahlbom.—Marignac determined the atomic weight of tantalum by purifying potassium tantalum fluoride (K_2TaF_7) by partial crystallisation, treating it with concentrated sulphuric acid, extracting the potassium sulphate thus formed with hot water, and igniting the residue, which consisted of a mixture of tantalum sulphate and tantalum acid. The Ta_2O_5 thus obtained was then weighed, and the potassium sulphate in the filtrate was also determined. The atomic weight was thence calculated to be 183. This method, however, is open to objection; for instance, fluorine is not included amongst those elements whose atomic weights are accurately known, and, moreover, it is very probable that on evaporation with sulphuric acid some of the tantalum passes away as fluoride. The authors have consequently undertaken a new determination. First or all they used potassium tantalum fluoride, but were not satisfied with the results, so fell back upon the conversion of the metal into oxide. Perfectly pure metal foil was cut up into small pieces and ignited in a platinum Rose's crucible in pure oxygen. As the mean of five experiments which agreed well among themselves it was found that $\text{Ta} = 181.0$. According to Bernoulli, an anode of tantalum metal is dissolved in strong alkali solution when an electric current is passed. The authors accordingly tried, by using a suitable silver salt solution in the circuit and comparing the weight of the tantalum dissolved with the weight of the silver separated, to find the equivalent of tantalum. The experiments, however, failed, because at low potentials the tantalum electrode was not attacked, and when the potential was raised, solution took place suddenly and large sparks were formed.

Titration of Hydrofluosilicic Acid.—N. Sahlbom and F. Willy Hinrichsen.—The authors have tested for fluorine the waters of the Bertscheid Springs, which contain large amounts of sulphur. They determined the fluorine by titrating the hydrofluosilicic acid formed on treating the silicon fluoride with water. They found that hydrofluosilicic acid is very readily split up hydrolytically in presence of alkalis, forming hydrofluoric acid and silicic acid. If, then, care is taken, by precipitating with alcohol, to remove the potassium or barium salt from the further action of the hydroxyl ions, the acid can be titrated directly as a dibasic acid, according to the equation $\text{H}_2\text{SiF}_6 + 2\text{KOH} = \text{K}_2\text{SiF}_6 + 2\text{H}_2\text{O}$. If the solution is warmed on the water-bath the titration can be performed with caustic soda without further addition of alcohol. In this case the reaction proceeds according to the equation $\text{H}_2\text{SiF}_6 + 6\text{KOH} = 6\text{KF} + \text{Si}(\text{OH})_4 + 2\text{H}_2\text{O}$. Thus, for every

atom of fluorine one molecule of alkali is used. Phenolphthalein or litmus can be used as an indicator. Employing this method the authors found that the waters examined contain only 0.0008 grm. of fluorine per litre.

Radio-activity of the Thermal Springs at Aix.—N. Sahlbom and F. Willy Hinrichsen.—The examination of the radio-activity of the thermal springs was performed with Engler and Sieveking's apparatus. A litre of the thermal waters was used, or 125 grms. of the solid. The radio-activity was exceedingly small, if the water was used hot as taken from the spring. After it had stood for some time the cooled liquid gave rather higher values. Some of the numbers obtained, taking into account the induced activity and the loss of potential on using distilled water, were as follows:—

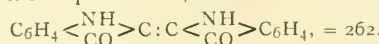
1 litre of water from—	Decrease in volt./hrs.	Remarks.
1. Krinolinen Spring (71°) ..	2	Straight from the Spring
2. Kaiser Spring (52°) ..	6	15 mins. after drawing
3. Krinolinen Spring (cooled) 20	1½	hours "
4. Kaiser Spring (cooled) ..	24	1 " "
5. Sebastian Spring ..	32	2 " "
6. Pocken Springs ..	76	2 " "

The authors also examined the mixtures of salts obtained on evaporating the waters, as well as clay, sinter, and mud. The following values were obtained:—

Substance (125 grms.).	Volt./hours.
1. Salt from Sebastian Spring ..	3.0
2. Clay from Sebastian Spring ..	8.0
3. Mud from Sebastian Spring ..	8
4. Sinter from Kaiser Spring ..	15
5. Sinter from Birtscheid ..	30
6. Mud from Krinolinen Spring ..	70
7. Mud from Kaiser Spring ..	483

As the surface of the layer has an important influence on radio-active action, on using smaller quantities a higher value of the decrease of potential was to be expected than when the whole 125 grms. was brought on to the apparatus at once, and thus the parts not on the surface could exert no action on the electroscope. As a matter of fact, an experiment with only 10 grms. of the mud from the Kaiser Spring, which showed the strongest activity, gave a fall of potential of 112 volts per hour. This would give 1400 volts per hour for 125 grms.

Molecular Weight of Indigo.—E. Beckmann and W. Gabel.—The reduction of indigo-blue to indigo-red, and thence to indigo-white, and also freezing-point determinations in *p*-toluidine and in phenol, indicate that the molecular weight of indigo is double that of the substance represented by Baeyer's simple formula,—



In view of the conflicting evidence upon this point the authors have determined the molecular weight afresh, firstly by means of ebullioscopic experiments, using Beckmann's apparatus, and for solvents quinoline, aniline, phenol, and *p*-toluidine. All the experiments gave as the result the simple molecular weight. The freezing-point experiments were then repeated, using aniline, phenol, and *p*-toluidine; only the last of these gave the doubled molecular weight.

Quantitative Sublimation of Phosphoric Acid from its Salts.—P. Jannasch and E. Heimann.—It has been observed that when phosphoric acid is determined by distilling a mixture of phosphate and carbon in a current of chlorine the results obtained are not satisfactory. If, however, an intimate mixture of phosphate and carbon is made by separating the latter from a sugar solution in the distilling flask by means of sulphuric acid, the phosphoric acid distils over quantitatively. This method was first tried with ammonium phosphate, when 99.65 per cent of the phosphoric acid passed over; it was then applied to the determination of phosphates in presence of fixed bases,

magnesium phosphate being used, and the results were equally satisfactory, after the distillation had been repeated several times.

Detection of Alkaline Earths by Means of Spectrum Analysis.—E. H. Riesenfeld and H. E. Wohlers.—The burner described by the authors in the *Chemiker Zeitung* (1906, xxx., 704) can be conveniently used to detect the alkaline earths. 0.1 to 0.5 grm. of the alkaline earth carbonate precipitate is dissolved in 0.5 to 1.0 c.c. 10 per cent hydrochloric acid and the solution made up to 2 c.c. with water. The current used is 0.2 ampère or with exceedingly dilute solutions 1 ampère. The lines used for the identification are:—

Ca = 622.0 μμ	553.5 μμ
Sr = 604.5 "	460.8 "
Ba = 524.2 "	513.7 "

To detect calcium and strontium the electrolytic method is more sensitive than the chemical, while in the case of barium the chemical method is to be preferred. The brightness of the lines enables an estimate to be made of the proportions of the metals present. The systematic analysis of the solutions of the carbonates of the alkaline earths is best performed by first examining by spectrum analysis. Even if barium is not detected it may be present in minute quantities, and the solutions must therefore be subsequently examined chemically.

Determination of Formic Acid with Potassium Permanganate.—Joseph Klein.—The author calls attention to the fact that he published some years ago details of a method of determining formic acid. By this method, which applies to the acid and its salts, the oxidation with permanganate was effected in boiling solution made feebly alkaline with caustic alkali; the excess of permanganate was decomposed with oxalic acid and dilute sulphuric acid, and the excess of oxalic acid was titrated with permanganate.

Cobaltic Dioximines.—L. Tschugaeff.—The author has prepared a series of complex compounds by the action of α-dioximes on salts of the metals belonging to the eighth group of the Periodic System. These compounds, which are called dioximines, contain the complex D_2H_2 or $2 \text{R.C:NO.H} - \text{H}_2$. The dioximines of cobalt are

very stable; the ammonia molecule of the complex base and its salts $[\text{Co}(2\text{NH}_3)\text{D}_2\text{H}_2]\text{X}$ can be replaced by a series of organic bases (e.g., methylamine, ethylamine, pyridine), and the resulting compounds are, as regards their properties and chemical behaviour, exactly analogous to the corresponding diamine salts.

Reactions at Low Temperatures.—Walter Peters.—Vorlander found when investigating the addition products of hydrochloric acid and unsaturated ketones at low temperatures, that the affinity increases in the cold. The author has now investigated the behaviour of organic bases towards hydrocyanic acid at the temperature of an ether-carbonic acid mixture. One molecule of the base was dissolved in 10 c.c. of absolute ether and rather more than one molecule of hydrocyanic acid in the same quantity of solvent; the solutions were cooled to -70° , and mixed. The resulting precipitate was poured without filtration on a tile over liquid air, and the ether completely drawn off in one-half to two hours. Thus the following cyanides were isolated or at least shown to be capable of existence:—Propyl ammonium cyanide, di-ethyl ammonium cyanide, tri-ethyl ammonium cyanide, di-methyl hydrazinium cyanide, pentamethylene diaminium cyanide, piperidinium cyanide, conitinium cyanide.

Molecular Weight of Hypophosphoric Acid.—Arthur Rosenheim, Wilhelm Stadler, and Felix Jacobsohn.—The acid sodium salt of this acid was prepared by immersing bars of yellow phosphorus in a solution of sodium acetate and keeping the whole at a temperature of from 6° to 8° . In six to eight days acid sodium hypophosphate had crystallised out. This was re-crystallised from water

containing acetic acid, and the formula was found to be $\text{NaHPO}_3 \cdot 3\text{H}_2\text{O}$. The molecular conductivities of a solution of the salt and of a solution of the salt containing an equivalent of sodium hydrate were then determined, and it was observed that NaHPO_3 behaves like an acid salt, and that the solution containing caustic soda undoubtedly contained hydroxyl ions. Hence no definite conclusions regarding the basicity of the salt could be drawn from these experiments. From the solidification curve of mixtures of H_3PO_3 and H_3PO_4 it was found that when phosphorous and phosphoric acid are fused together hypophosphoric acid is not formed, and hence it is probably not a condensation product of these two acids. The molecular raising of the boiling-point was then determined for hypo-phosphoric acid methyl ester and pyro-phosphoric acid ethyl ester, using as solvents ethyl iodide, ethyl bromide, and chloroform, and the results showed that the hypo-phosphoric acid ester has the simple molecular formula $(\text{CH}_3)_2\text{PO}_3$, and that the acid itself is therefore to be regarded as a derivative of tetravalent phosphorus and not as a derivative of tri- and penta-valent phosphorus with the formula $\text{H}_4\text{P}_2\text{O}_6$. The parallel experiments with the pyrophosphoric acid ester showed that the solvents used behave normally in determinations of the molecular weight of esters.

Hydrosol of Thorium Oxide Hydrate.—Arthur Miller.—This hydrosol can be prepared by precipitating thorium hydroxide with alkali from a solution of the nitrate in water, washing the precipitate very carefully to remove all electrolytes, and heating it with water to boiling, meanwhile shaking well. A further portion of the dried nitrate is dissolved in water and added to the hydroxide from a burette, the boiling being continued for five minutes between each addition. Thus a perfectly homogeneous hydrosol is obtained, which is unaltered on boiling. On evaporation of the solution a glittering brittle crust is obtained which swells up on addition of water, and gradually dissolves to an opalescent hydrosol. Thus the change of state is reversible, and the dry residue is the solid hydrosol of thorium hydroxide. The addition of neutral salts does not alter the hydrosol. Alkalis give with it a gelatinous transparent precipitate, and the insoluble hydrosol is also formed by the addition of most acids.

Compounds of Stannic Sulphate with Sulphates of the Alkaline Earths and with Lead Sulphate.—R. F. Weinland and Hugo Köhl.—If to a solution of orthostannic acid in concentrated sulphuric acid is added a solution of calcium sulphate in the same acid, and the mixture is concentrated by slow evaporation in a porcelain dish, small colourless cubes of $\text{Sn}(\text{SO}_4)_2 \cdot \text{CaSO}_4 \cdot 3\text{H}_2\text{O}$ separate out. The ortho-stannic acid must be freshly prepared, and the calcium sulphate is best precipitated from boiling calcium chloride solution with dilute sulphuric acid, washed, and used without drying. With strontium, barium, and lead sulphates the stannic sulphate forms corresponding compounds. The salts of the alkali sulphates are more difficult to isolate, and the authors are still engaged in research upon them. The stannic alkaline earth sulphates appear to be stannates the oxygen of which is replaced by SO_4 :— SnO_3Ca , $\text{Sn}(\text{SO}_4)_2\text{Ca}$: they are insoluble in water, and when boiled with water partially decompose, yielding stannic acid and sulphate of the alkaline earth. The calcium and strontium salts dissolve in excess of hot concentrated hydrochloric acid; when the barium salt is boiled with hydrochloric acid all the barium separates out as sulphate and the stannic acid goes into solution.

Electrolytic Determination of Copper.—F. Foerster.—The author uses for his electrolyte 100 c.c. of a solution of copper sulphate containing 10 c.c. of 2-N sulphuric acid, the cathode being a cylindrical Winkler's wire gauze cathode, and the anode a platinum wire spiral in the axis of the cathode, and a lead accumulator is short-circuited by this bath. No gaseous hydrogen is evolved, and the method is simple and accurate. If the electrolyte is

warmed to 70° the separation is greatly hastened; thus with 2 volts in about an hour 0.15 grm. of copper can be quantitatively separated, using a sulphuric acid solution.

Halogen Salts of Niobium Oxychloride (NbOCl_3) and of Niobium Oxybromide.—R. F. Weinland and Ludwig Storz.—The authors have obtained two series of salts:—(1) $\text{NbOCl}_3 \cdot \text{RCl}$, (2) $\text{NbOCl}_3 \cdot 2\text{RCl}$, and the corresponding bromides. To prepare these salts a solution of hydrated niobic acid in hydrochloric or hydrobromic acid, or of niobium oxychloride or pentachloride in absolute alcohol is used. The addition of solutions of quinoline, pyridine, caesium, and rubidium chlorides in concentrated hydrochloric acid to these solutions gave the following chloro-salts:— $\text{NbOCl}_3 \cdot \text{C}_9\text{H}_7\text{NHCl}$, $\text{NbOCl}_3 \cdot \text{C}_5\text{H}_5\text{NHCl}$, &c. The chloro-salts are colourless or faint yellow colour. They crystallise well, the caesium and rubidium salts regularly. They are decomposed in moist air, giving up hydrochloric acid, and with water they split up, yielding niobic acid. The bromo salts, which are red in colour, are still more unstable than the chlorides, giving up hydrobromic acid and turning white in moist air. They also are decomposed by water.

Transference of Oxygen by Burning Potassium.—K. A. Hofmann and H. Hiendlmaier.—When potassium is fused and burnt in a current of air it is found that almost all materials are strongly attacked. For instance, lead and gold are converted into potassium platinate and potassium aurate; pure silver is comparatively little affected, while copper, iron, nickel, and cobalt are strongly oxidised. If pure potassium is burnt on pure nickel-foil, on cooling a mixture of yellowish brown potassium peroxide with long black prisms is formed. When the mass is introduced into ice-cold water, the potassium peroxide splits up into caustic potash and oxygen, and a black crystalline powder sinks to the bottom. This powder has the composition represented by the formula $\text{Ni}_2\text{O}_5\text{H}_4$. It has a strong oxidising action on organic substances; thus it converts alcohol into aldehyde in presence of sulphuric acid. It is also reduced by cellulose, and therefore cannot be collected on filter-paper without losing some of its oxygen. The constitution appears to be expressed by $\text{NiO}_2 \cdot \text{NiO} + 2\text{H}_2\text{O}$, and the compound is thus a nickelo-nickelite. The authors have also prepared a similar cobalto-cobaltite, $\text{CoO} \cdot 2\text{CoO}_2 \cdot 2\text{H}_2\text{O}$. This compound is far more stable than the nickelo-nickelite. It is not attacked by dilute sulphuric acid in the cold, and even the concentrated acid does not liberate oxygen until the substance is heated. Strong hydrochloric acid, however, liberates chlorine.

MISCELLANEOUS.

The Fogging of Plates in Tropical Climates.—Referring to Mr. McDowall's paper in the *CHEMICAL NEWS* for November 2nd (vol. xciv., p. 209), Dr. W. J. Russell, F.R.S., writes to say that the points mentioned in Mr. McDowall's paper have already been described by him; and even the spoiling of some of the plates used at the last eclipse expedition was explained by him in a letter to *Nature* last December.

Royal Institution.—A Christmas Course of Lectures, adapted to a juvenile auditory, will be delivered at the Royal Institution by Mr. W. Duddell, on "Signalling to a Distance—from Primitive Man to Radio-telegraphy" (experimentally illustrated). The dates of the lectures are December 27, 29, 1906, January 1, 3, 5, 8, 1907, at three o'clock.

Chemical Abstracts of the American Chemical Society.—In accordance with the recent vote of the Society the publication of a semi-monthly abstract journal will be commenced January 1, 1907. The corps of those in charge of the various divisions of the journal is already

well organised and work upon the abstracts has been commenced. It is intended to include in the Journal abstracts of all new work in chemistry published in the world after October 1, 1906. Chemical patents issued in the United States, Germany, France, and England, after July 1, 1906, will be included. The abstracts will be classified under the following divisions, the selection of abstractors and the oversight of each division being placed in the hands of the persons named:—

Apparatus. W. H. Walker.
General and Physical Chemistry. G. N. Lewis.
Photography. L. H. Friedburg.
Electro-chemistry. W. R. Whitney.
Radio-activity. H. N. McCoy.
Inorganic Chemistry. Alexander Smith.
Analytical Chemistry. L. M. Dennis.
Mineralogical and Geological Chemistry. W. F. Hillebrand.
Metallurgy. J. W. Richards, Henry Fay.
Acids, Alkalis, and Salts. T. L. Briggs.
Glass and Pottery. G. E. Barton, Albert V. Bleining.
Cements and Mortars. Harry Drew.
Fuel, Gas, Coke. J. D. Pennock.
Organic Chemistry. M. T. Bogert.
Petroleum, Asphalt, Turpentine, Wood Products. S. S. Sadtler.
Cellulose, Paper. A. D. Little.
Explosives. C. E. Munroe.
Dyes, Textile Fabrics, Bleaching, Inks. L. A. Olney.
Pigments, Resins, Varnishes, Indiarubber. A. H. Sabin.
Fats, Fatty Oils, and Soap. W. D. Richardson.
Sugar, Starch, and Gum. C. A. Browne, Jun.
Leather, Glue. J. H. Yocum.
Biological Chemistry. L. B. Mendel.
Foods. W. D. Bigelow.
Nutrition. C. F. Langworthy.
Water, Sewage, Disinfectants, Insecticides. L. P. Kinnicutt.
Fermented and Distilled Liquors. Robert Wahl.
Pharmaceutical Chemistry. A. B. Stevens.
Soils and Fertilisers. F. P. Veitch, J. H. Pettit.
Patents. W. H. Seaman.

The dues of the Society for 1907 will be increased to eight dollars to pay for the expense of the new publication. It is expected that for the first year or two, at least, the cost of the abstract journal will be considerably greater than the increased receipts from dues, and the success of the enterprise depends upon the hearty support of our members in maintaining and increasing the membership of the Society. It is therefore urged that every member of the Society shall make an especial effort to secure an increase in the membership. The abstract journal will be published twice a month. The Journal of the American Chemical Society will, of course, be continued and will contain original articles, book reviews, and reviews of recent progress in the various fields of chemistry. For those who are not members of the Society the subscription price will be as follows:—*Journal of the American Chemical Society*, monthly, six dollars; *Chemical Abstracts*, semi-monthly, six dollars; for both journals, sent to the same subscriber, ten dollars.

MEETINGS FOR THE WEEK.

MONDAY, 19th.—Society of Arts, 8. (Cantor Lectures). "Artificial Fertilisers—their Nature and Functions," by A. D. Hall.
WEDNESDAY, 21st.—Microscopical, 8. "Use of a Top Stop for Developing Latent Powers of the Microscope," by J. W. Gordon.
— Society of Arts, 8. Opening Address of the One Hundred and Fifty-third Session, by Sir Steuart Colvin Bayley, K.C.S.I., &c.
FRIDAY, 23rd.—Physical, 5. "On the Electrical Radiation from Benetennæ," by J. A. Fleming. "Auroral and Sunspot Frequencies contrasted," by C. Chree. "Electrical Resistance of Alloys," by R. S. Willows.

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MATHEMATICS E. H. SMART, M.A.
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THE CHEMICAL NEWS.

VOL. XCIV., No. 2452.

RELATIONSHIP BETWEEN THE ATOMIC WEIGHTS OF ANALOGOUS ELEMENTS.

By E. BRADBURY.

IN the CHEMICAL NEWS of September 28, 1906 (vol. xciv., p. 157), I attempted to show that the properties of the elements and of their compounds are accurately indicated by their specific gravities, and also pointed out that elements grouped together in my classification frequently showed numerical relationships in their atomic weights. In this note I intend to deal with the latter point more fully.

Let W be atomic weight. Then—

$$\frac{W \text{ Rd}}{W \text{ Ba}} = \frac{W \text{ Ca}}{W \text{ Mg}} = \frac{W \text{ Zn}}{W \text{ Ca}} = \frac{W \text{ Pd}}{W \text{ Zn}} = \frac{W \text{ Pt}^*}{W \text{ Sn}} = \frac{W \text{ Sn}}{W \text{ Ge}} = \left(\frac{W \text{ Mg}}{W \text{ Be}} \right)^{\frac{1}{2}};$$

also—

$$\frac{W \text{ Pb}}{W \text{ Ba}} = \left(\frac{W \text{ Ba}}{W \text{ Ca}} \right)^{\frac{1}{2}}.$$

Similarly—

$$\left(\frac{W \text{ Pb}}{W \text{ Sr}} \right)^{\frac{1}{2}} = \frac{W \text{ Sr}}{W \text{ Zn}} = \left(\frac{W \text{ Si}}{W \text{ C}} \right)^{\frac{1}{2}} = \left(\frac{W \text{ Sn}}{W \text{ Si}} \right)^{\frac{1}{2}}$$

and—

$$\left(\frac{W \text{ Th}}{W \text{ Pd}} \right)^{\frac{1}{2}} = \frac{W \text{ Pd}}{W \text{ Ge}}.$$

Considering the trivalent elements, we get—

$$\left(\frac{W \text{ Ir}}{W \text{ Cr}} \right)^{\frac{1}{2}} = \frac{W \text{ Cr}}{W \text{ Al}}; \quad \frac{W \text{ In}}{W \text{ Fe}} = \frac{W \text{ Fe}}{W \text{ Al}};$$

$$\frac{W \text{ Ta}}{W \text{ Sb}} = \left(\frac{W \text{ Sb}}{W \text{ V}} \right)^{\frac{1}{2}}; \quad \frac{W \text{ Ir}}{W \text{ Ce}} = \frac{W \text{ Ce}}{W \text{ Rh}} = \frac{W \text{ Rh}}{W \text{ As}};$$

$$\frac{W \text{ Ta}}{W \text{ In}} = \frac{W \text{ In}}{W \text{ Ga}} = \frac{W \text{ Ga}}{W \text{ Sc}} = \frac{W \text{ Sc}}{W \text{ Al}} = \frac{W \text{ Ir}}{W \text{ Sb}} = \frac{W \text{ Sb}}{W \text{ As}};$$

$$\frac{W \text{ Bi}}{W \text{ Ce}} = \frac{W \text{ Ce}}{W \text{ Nb}} = \left(\frac{W \text{ P}}{W \text{ N}} \right)^{\frac{1}{2}}.$$

It is interesting to note that similar relationships exist with radicles, *e.g.*,—

$$\frac{W \text{ Rb}}{W \text{ K}} = \frac{W \text{ K}}{W \text{ Am}}; \quad \frac{W \text{ F}}{W \text{ Cu}} = \frac{W \text{ Cu}}{W \text{ Cl}}; \quad \frac{W \text{ N}_3}{W \text{ Br}} = \left(\frac{W \text{ Cl}}{W \text{ I}} \right)^{\frac{1}{2}}.$$

Mercury is analogous to Cd and Cu; the following relationships verify it:—

$$\frac{W \text{ Hg}}{W \text{ Cd}} = \frac{W \text{ Cd}}{W \text{ Cu}}.$$

The following ratios, like the foregoing, are, in my opinion, indicative that analogous elements have a common origin:—

$$\frac{W \text{ O}}{W \text{ S}} = \frac{W \text{ S}}{W \text{ Cu}} = \left(\frac{W \text{ Cu}}{W \text{ Zr}} \right)^2 = \left(\frac{W \text{ Zr}}{W \text{ Te}} \right)^2.$$

$$\frac{W \text{ U}}{W \text{ Mo}} = \left(\frac{W \text{ Mo}}{W \text{ Cr}} \right)^{\frac{3}{2}}; \quad \left(\frac{W \text{ Os}}{W \text{ Zr}} \right)^{\frac{1}{2}} = \left(\frac{W \text{ Zr}}{W \text{ Mn}} \right)^{\frac{1}{2}}.$$

$$\frac{W \text{ W}}{W \text{ Se}} = \left(\frac{W \text{ Se}}{W \text{ Cr}} \right)^2.$$

Bradbury's School,
16, John Dalton Street, Manchester,
November 9, 1906.

ON THE

CHEMICAL ACTION OF ULTRA-VIOLET LIGHT.

By W. H. ROSS.

THE work herein described was undertaken with a view to making especially some quantitative measurements on the chemical action of light. Since in the majority of chemical changes the greatest effect is produced by ultra-violet light, it was thought advisable to work with a source of light rich in these rays. Such a source was obtained by causing an oscillatory spark to pass between aluminium terminals joined in the secondary circuit of a large induction coil used as a transformer. In the secondary circuit was also joined in parallel a large Leyden jar. Through the primary circuit was passed an alternating current of 110 volts having a strength of 3.4 amperes. To obtain a constant source of light proved a matter of considerable difficulty. However, by arranging an apparatus as thus described, and having in the primary circuit an ammeter and resistance boxes, the resistance could be changed at will and the strength of the current thus kept constant. When a uniform current was in this way maintained, the amount of energy given out by the spark during intervals of ten minutes was practically constant. This was shown to be the case by the fact that the same amount of iodine was set free from equal volumes of a potassium iodide solution, when exposed to the light under exactly the same conditions for equal intervals of time. After every observation the aluminium terminals were sharpened, and then placed the same distance apart so that every exposure might be begun under the same conditions. The terminals used were large—3 m.m. by 8 m.m. cross-section—and were allowed to rest for the greater part of their length on iron plates placed 7 c.m. apart. In this way the heat generated by the spark was rapidly conducted away. By placing the proper amount of ice in small dishes resting on the terminals, the temperature of a solution of 3 c.c., placed in a cell directly underneath the spark, could be kept within a range of 1° during an exposure of ten minutes.

Aluminium terminals were used on account of the strong ultra-violet rays given out by a spark passing between them. The rate of decomposition produced by the light in the case of the iodides, when terminals of aluminium were used, was found to be at least twice as great as that resulting when terminals of any of the other common metals are used. Cadmium could not be used on account of its softness. An accurate comparison of the decomposition produced, when electrodes of different metals were used, was not made, since, on account of their difference in hardness, the experiments could not be carried out under comparable conditions.

Decomposition of the Iodides.

The compounds first investigated were the iodides of the different metals in solution. The solution to be exposed to the light was placed in a shallow vessel directly underneath the spark. The amount of iodine set free was determined by titrating with a standard solution of sodium thiosulphate, using starch as indicator. When making exposures of ten minutes, the most convenient strength of the sodium thiosulphate was found to be 1/1000 normal. With a solution of this strength the amount of iodine set free could not be determined by titrating with the thiosulphate directly. By adding an excess of the thiosulphate solution, however, and then titrating with a 1/1000 normal solution of iodine, the amount of iodine set free could be accurately determined.

It was noticed when making titrations that the purest water obtainable, that used in this laboratory for making electrical conductivity measurements, had the power of decolorising quite an appreciable amount of iodine. Thus, to 20 c.c. of water, containing a few drops of starch solution, had to be added from 0.2 c.c. to 0.4 c.c. of a

1/1000 normal solution of iodine before any blue colour appeared. With an iodide present a less amount of the iodine solution was required. Hence, before titrating any solution exposed to the light, a blank titration of a solution containing the same amount of iodide was made in every case, in order that the proper correction to be applied might be found.

When a solution of potassium iodide was exposed to the light in an open vessel, the amounts of iodine set free, on making exposure for equal intervals of time, varied greatly. When the distance of the solution from the spark was doubled, the rate of decomposition remained almost the same as before. The spark was then made to pass through an atmosphere of oxygen. This was done by placing the terminals in a large bell-jar filled with the gas. Under these conditions, the rate of decomposition was found to be very much increased. In replacing the oxygen with carbon dioxide, the amount of decomposition resulting in the same length of time was very small. It therefore became evident that the greater part of the decomposition first obtained was produced, not by the light only, but principally by the action of ozone and the oxides of nitrogen formed by the passage of the spark through air.

To determine the effect of the ultra-violet light only, the solution was placed in a small shallow dish provided with a quartz cover. The latter was sealed into a rim of hard rubber, which was in turn surrounded by an elastic rubber band. This then could be slipped over the top of the dish so as to secure the complete exclusion of any gas. When the dish was now placed underneath the spark, the decomposition resulting represented the total effect of the waves of light given out by the spark. By subtracting from this the effect produced when a thick piece of glass plate was interposed between the spark and the solution, the effect of the ultra-violet light alone, or that part of it capable of being absorbed by the glass, was determined. When a photograph of the spectrum given by the spark was taken by means of a spectroscope, it was found that, when the glass plate used in the following experiments was interposed between the spark and the spectroscope, all wave-lengths were absorbed below λ 3260.

That the decomposition of the iodide, which took place when gases formed by the spark were excluded, was due to the action of the light alone was shown by varying the distance of the solution from the spark. It was now found that the amount of iodine set free varied inversely as the square of the distance, which one would expect if the decomposition is due entirely to the amount of light energy incident upon the solution. When making exposures, 3 c.c. of the solution were taken in every case, while the time of exposure was ten minutes.

The effect produced on solutions of potassium iodide of different concentrations is shown in the following table:—

Grm.-mol. KI per litre.	I set free measured in c.c. of N/1000 solution.
3.0	3.58
2.0	3.35
1.0	3.00
0.5	2.68
0.2	2.15
0.1	1.85
0.05	1.50
0.02	1.15
0.01	1.00
0.005	0.80
0.002	0.50
0.001	0.40

Duplicate observations, which agreed with one another within 0.1 c.c., were made in every case.

On varying the time of exposure, the amount of iodine set free was not at first exactly proportional to the time. This agrees with what might be expected, for the colour of the solution—or its power of absorption—changes after a

short exposure. A tenth-normal solution was used in each case.

Time of exposure.	I set free in c.c. of N/1000 solution.
10	1.85
20	3.30
30	4.90

When making these observations, the terminals were sharpened and placed the same distance apart every ten minutes.

When the glass plate already referred to was interposed between the spark and the solution the amount of iodine set free was very small. Thus, in the case of a twice normal solution of potassium iodide, the amount set free was found to be equivalent to only 0.15 c.c. of a 1/1000 normal solution of iodine, while in the case of a 1/10 normal solution no free iodine could be detected after an exposure of ten minutes. When working with the more concentrated solution, the amount of iodine set free by the action of the visible light was subtracted from the total amount set free to get the results given above.

The iodides of sodium, lithium, barium, calcium, and zinc were next investigated, but all were found to give the same results as those given by potassium iodide.

Grm.-equivalents of iodide per litre.	Iodine set free in c.c. of N/1000 solution.					
	KI.	NaI.	LiI.	BaI ₂ .	CaI ₂ .	ZnI ₂ .
2.0	3.35	3.40	3.35	3.45	3.37	3.40
0.5	2.68	2.60	2.65	2.70	2.73	2.70
0.1	1.85	1.80	1.85	1.75	1.80	1.85
0.01	1.00	1.00	1.05	1.00	1.03	1.00

These observations were made at a temperature of 18°. A variation, however, in the temperature of any of the solutions between 15° and 30° produced no appreciable change in the rate of decomposition.

Reduction of Ferric Salts.

Solutions of the sulphate, nitrate, and chloride were standardised by reducing with stannous chloride and then titrating with potassium permanganate in the presence of manganese sulphate and phosphoric acid. That the solutions thus standardised as regards the iron also contained equivalent amounts of acid was shown by titrating a definite portion of each solution with a standard sodium hydroxide solution, using phenolphthalein as indicator.

When two Nessler tubes surrounded with white paper were filled with the standard sulphate and chloride solution, it was noticed that the first solution was slightly darker than the second, but on adding to it a few drops of acid it could be brought to the same colour as the other when thus viewed by reflected light. When the tubes, with the paper coverings removed, were placed so as to view the solutions by transmitted light, the sulphate solution was now much lighter in colour than the chloride solution; this shows that the two solutions have a different power of absorption for light. Hence, when acted upon by light of the same intensity, it was found—as might be expected for this reason alone—that the solutions were not reduced at the same rate.

As is well known, the action of light on ferric salts is very much increased when there is present in solution some organic compound (as cane-sugar) which of itself will not reduce the salts, but does so under the influence of light. Hence, when working with these solutions, a definite amount of sugar was always added.

The amount of salt reduced was determined by titrating with a standard 3/400 normal solution of potassium permanganate. When finding the effect of ultra-violet light on solutions of different strength, a one-fifth normal solution was first taken, to which was added 10 grms. of sugar per 50 c.c. of solution. A one-tenth normal solution was then prepared by adding to a definite volume of the one-fifth normal solution an equal volume of water. Solutions of other dilution were prepared from the one-fifth normal solution in the same way.

With ferric chloride, sulphate, and nitrate the following results were obtained on making exposures of ten minutes.

Grm.-equivalents of salt per litre.	Ferrous salt formed in c.c. of 3N/400 solution.		
	FeCl ₂ .	FeSO ₄ .	Fe(NO ₃) ₂ .
0.20	2.50	2.45	0.55
0.10	2.25	1.70	0.50
0.05	1.93	1.05	0.48
0.02	1.27	0.50	—
0.01	0.85	0.40	—
0.005	0.70	—	—
0.002	0.60	—	—

The amount of sugar added has a considerable effect on the amount of reduction which takes place, as is shown thus:—

Percentage of sugar added.	FeCl ₂ formed in c.c. of 3N/400 solution.
10	1.73
20	2.50
40	3.22

The amount of ferric salt reduced is approximately proportional to the time of exposure. A one-fifth normal solution of ferric chloride containing 10 grms. of sugar per 50 c.c. of solution gave results as follows:—

Time of exposure (minutes).	FeCl ₂ formed in c.c. of 3N/400 solution.
10	2.53
20	4.70
30	7.15

Varying the temperature of any ferric salt solution was found to have a slight effect on the rate of reduction.

Reduction of Chlorates and Bromates.

While solutions of the chlorates and bromates are quite stable in sunlight, they were found to be reduced to quite an extent when acted upon by that part of the ultra-violet spectrum capable of being absorbed by glass. The extent of the reduction was determined by titrating the amount of chloride or bromide formed by means of a 1/200 normal solution of silver nitrate. It was found that solutions of all chlorates of the same strength were reduced at the same rate, while the same thing was true of the bromates. The rate of reduction of the chlorates, however, differed from that of the bromates. Unlike the iodides or ferric salts, varying the strength of either the chlorate or bromate solutions from one-half to one-fiftieth normal did not produce any appreciable difference in the amount of reduction which took place.

Grm.-equivalents of KClO ₃ [or NaClO ₃ , Ba(ClO ₃) ₂ , &c.] per litre.	Chloride formed in c.c. of N/200 solution.
0.50	0.80
0.10	0.80
0.02	0.80
0.01	0.78

In the case of the bromates the amount of salt reduced was less than in the case of the chlorates. Thus, when the strength of any standard bromate solution was varied from one-half to one-hundredth normal, the amount of bromide formed in every case was equivalent to only 0.25 c.c. of a 1/200 normal silver nitrate solution.

The amount of chlorate or bromate reduced was found to be exactly proportional to time of exposure.

Sugar added to solutions of the chlorates or bromates resulted in an increase in the amount of reduction which took place, but to a much less extent than in the case of the iron salts. Varying the strength of the solution now produced a change in the amount of reduction. A one-half normal solution of potassium chlorate containing 10 grms. of sugar per 50 c.c. of solution, when diluted so as to make a one-twentieth normal solution, gave the same results, however, as one containing no sugar.

Grm.-mol. of KClO ₃ per litre.	Chloride formed in c.c. of N/200 solution.
0.5	1.50
0.2	1.15
0.1	0.90
0.05	0.80
0.01	0.80

When sugar was added to the bromate solutions a greater amount of reduction took place than in the case of the chlorates.

Grm.-mol. of bromate per litre.	Bromide formed in c.c. of N/200 solution from—		
	KBrO ₃ .	NaBrO ₃ .	Ba(BrO ₃) ₂ .
0.5	1.75	1.73	1.75
0.2	1.55	1.50	1.55
0.1	1.40	1.42	1.37
0.05	1.20	1.20	1.25

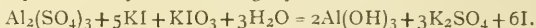
Before making a titration to determine the amount of change produced in any particular solution, a blank titration was first made in every case.

I wish to express my thanks to Professors Jones and Wood, at whose suggestion this work was undertaken.—*Journal of the American Chemical Society*, xxviii., No. 6.

THE IODOMETRIC DETERMINATION OF ALUMINIUM IN ALUMINIUM CHLORIDE AND ALUMINIUM SULPHATE.

By S. E. MOODY.

A PROCESS for the gravimetric determination of alumina in salts of aluminium has been described by Stock (*Ber.*, 1900, xxxiii., [1.], 548), who bases the method upon the reaction represented by the following equation:—



This equation would show that iodine is liberated when potassium iodate and potassium iodide are together added to a solution of aluminium sulphate. It was found, however, that in the action of the iodide-iodate mixture upon a solution of potassium alum, only about two-thirds of the iodine corresponding to the aluminium salt is accounted for; and this suggests that the reaction is not completed according to the equation, and that the precipitate formed is not the simple hydroxide. Upon ignition the precipitate yields, however, the total amount of alumina present; and, since the character of the precipitate is good, the process is easily managed, and gives, as Stock has said, an excellent gravimetric method for the determination of alumina.

Taking aluminium chloride, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, and proceeding in the same manner, similar results are obtained, and after dissolving the precipitate in sulphuric acid and adding silver nitrate to the dilute solution, a decided precipitate of silver chloride is observed, which upon washing, drying, and weighing is found to be about one-third of the amount of that substance corresponding to the original aluminium chloride. This indicates that it is an oxychloride which is formed on the addition of potassium iodide and iodate; moreover, upon removing by sodium thiosulphate the iodine first set free in the action and allowing the mixture to stand, progressive hydrolysis takes place as shown by the return of colour due to iodine, and this change can be still further hastened by heating after adding an excess of sodium thiosulphate to take up the iodine as liberated. The attempt was made therefore to complete the reaction between the iodide-iodate mixture and the aluminium chloride, or alum, by heating the solution in a Voit flask through which steam or, still better, hydrogen was passed, as an aid in the transfer of the iodine liberated to a receiver charged with a solution of potassium iodide. The iodine collected was titrated with $n/10$ sodium thiosulphate.

Table I. gives results obtained by this method. The

details of the experiments in which steam was used as an agent to force the iodine over are given in Section A, while those of the experiments in which hydrogen was employed are indicated in Section B.

TABLE I.

Approx. $n/10$ aluminium chloride solution.	HIO_3 .	KI.	Time.	Approx. $n/10$ $\text{Na}_2\text{S}_2\text{O}_3$.	Al_2O_3 cal- culated.	Diff.
C.c.	Grm.	Grm.	Mins.	C.c.	Grm.	Grm.
A.						
25	0.3	1.0	25	25.05	0.0427	-0.0007
25	0.3	1.0	90	25.15	0.0428	-0.0006
B.						
25	0.3	1.0	20	25.05	0.0427	-0.0007
25	0.3	1.0	15	25.10	0.0428	-0.0006
25	0.3	1.0	15	25.00(a)	0.0426	-0.0009
25	0.3	1.0	15	25.00(a)	0.0426	-0.0009

(a) New standard.

In each of these experiments the iodide-iodate mixture was made by exactly neutralising iodic acid with potassium hydroxide, adding a minute crystal of the iodic acid, introducing the potassium iodide in solution, and taking up with a drop or two of sodium thiosulphate the iodine set free. This mixture was put into the Voit flask together with the aluminium chloride, and the whole was heated in the current of steam or hydrogen.

Applying the process to a solution of potassium alum the results recorded in the following table were obtained:—

TABLE II.

Approx. $n/10$ aluminium potassium alum.	KIO_3 .	KI.	Time.	Approx. $n/10$ $\text{Na}_2\text{S}_2\text{O}_3$.	Al_2O_3 cal- culated.	Al_2O_3 found.	Diff.
C.c.	Grm.	Grm.	Mins.	C.c.	Grm.	Grm.	Grm.
25	0.3	1.0	30	24.55	0.0410	0.0414	-0.0004
25	0.3	1.0	30	24.60	0.0411	0.0416	-0.0005
25	0.3	1.0	25	24.50	0.0409	0.0414	-0.0005
25	0.3	1.0	30	24.70	0.0413	0.0416	-0.0003
25	0.3	1.0	35	24.50	0.0409	0.0415	-0.0006
25	0.3	1.0	30	24.55	0.0410	0.0415	-0.0005
25	0.3	1.0	25	24.50	0.0409	0.0415	-0.0006

In Table III. are shown results of the application of the process to an ammonium alum.

TABLE III.

Approx. $n/10$ ammonium alum.	KIO_3 .	KI.	Time.	Approx. $n/10$ $\text{Na}_2\text{S}_2\text{O}_3$.	Al_2O_3 cal- culated.	Diff.
C.c.	Grm.	Grms.	Mins.	C.c.	Grm.	Grm.
25	0.3	1.0	20	25.20	0.0429	+0.0007
25	0.3	1.0	15	25.17	0.0429	+0.0007
25	0.3	1.0	20	25.10(b)	0.0427	+0.0005
25	0.3	1.0	25	25.20(b)	0.0429	+0.0007
25(a)	0.3	1.0	12	25.70(b)	0.0421	-0.0001
25(a)	0.3	1.0	12	24.65(b)	0.0420	-0.0002
25	0.3	1.0	20	25.20(c)	0.0430	+0.0008
25	0.3	1.0	25	25.15(c)	0.0429	+0.0007
25	0.3	2.0	25	25.20(c)	0.0430	+0.0008
25	0.3	2.0	20	25.15(c)	0.0429	+0.0007

(a) Liquid in Voit flask not clear.

(b) New standard.

(c) New standard.

These results proved to be too high, and led to the conclusion that the ammonium sulphate was acted upon by the iodic mixture, liberating an additional portion of iodine. Experiments with ammonium sulphate verified the supposition, and the process is therefore less accurate in the presence of ammonium salts. In fact, ammonium sulphate

in the amounts taken may be completely hydrolysed in the course of three hours, about one-half of the iodine liberated by the sulphuric acid formed in the hydrolysis being available for estimation under the conditions of the foregoing determinations. When, however, the distillate is collected in a solution of potassium iodide containing sufficient acid to combine with the ammonia volatilised, iodine is liberated in amount equivalent to the entire quantity of sulphates present, and may be titrated with sodium thiosulphate.

The reaction between iodine and ammonia in alkaline solution, and the hydrolysis of ammonium salts, are undergoing further investigation by the writer.

The attempts to obtain a complete reaction by heating the mixture in a pressure bottle showed that the results of this procedure are low, although but slightly deficient, and cannot be used for estimating correctly the amount of aluminium salt in the solution.

The following method can be recommended as one giving constant results which correspond closely with the gravimetric determinations and the theoretical amount of alumina in neutral aluminium chloride, sulphate, or alum, little time being necessary for a single determination:—

Measure 25 c.c. of the approximately $n/10$ solution of the neutral aluminium salt to be analysed into a Voit flask, and to this add a mixture of 10 c.c. of a solution of neutral potassium iodate (30 grms. to a litre), and 1.0 grm. potassium iodide. Pass a current of hydrogen through the liquid, and heat for fifteen to twenty-five minutes, or until the solution is nearly colourless, collecting the iodine liberated in a Drexel flask, about half full of water, in which 3 grms. of potassium iodide is dissolved. Titrate with sodium thiosulphate the iodine in the Drexel flask and that which remains in the solution in the Voit flask, and calculate the amount of alumina, Al_2O_3 , corresponding to the iodine, 61, liberated.

The writer wishes to thank Prof. F. A. Gooch for friendly assistance during this investigation.—*American Journal of Science*, xx., p. 181.

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.*

By GREGORY PAUL BAXTER, MURRAY ARNOLD HINES,
and HARRY LOUIS FREVERT.

(Concluded from p. 237).

Method of Analysis (continued).

THE average of these results is almost identical both with that obtained in the previous analysis of cadmium chloride, 112.469, and with that obtained from the bromide, 112.467; hence it is evident that no serious error was introduced in our earlier work by the use of phosphorus pentoxide for drying hydrochloric acid gas. Furthermore, in other analyses of chlorides in this laboratory, where the salts were fused in an atmosphere containing hydrochloric acid, either the salt employed was initially anhydrous, so that it could not have taken up the phosphorus, as in the case of magnesium ammonium chloride (Richards and Parker, *Proc. Amer. Acad.*, 1896, xxxii., 55), and of strontium chloride (Richards, *Ibid.*, 1905, xl., 603), or else the concentrations of hydrochloric acid gas were so low that no error could have been introduced through the use of the hydrochloric acid, as in the case of calcium chloride (Richards, *Journ. Am. Chem. Soc.*, 1902, xxiv., 374).

Although Bailey and Fowler attribute to hydrobromic acid an effect similar to that of hydrochloric acid, for several reasons it is certain that in the experiments upon cadmium bromide described in the earlier part of this paper no appreciable amount of phosphorus was introduced into the salt by the action of the hydrobromic acid upon the

* From the *Journal of the American Chemical Society*, xxviii., No. 6.

THE ATOMIC WEIGHT OF CADMIUM.

Ag = 107.930. Cl = 35.473 (a).

No. of analysis.	Weight of CdCl ₂ in vacuum (grms.).	Weight of residue (grm.).	Loss in weight of boat (grm.).	Weight of Ag in vacuum (grms.).	Weight of AgCl in vacuum (grms.).	Weight of Ag added or subtracted (grm.).	Loss on fusion (grm.).	Weight of asbestos from filtrate (grm.).	Weight of AgCl from wash-waters (grm.).	Corrected wt. of CdCl ₂ (grms.).	Corrected weight of Ag (grms.).	Corrected wt. of AgCl (grms.).	Atomic weight of cadmium.
17.	5.62511	0.00015	0.00004	6.61993	—	0.00000	—	—	—	5.62500	6.61193	—	112.472
18.	6.81040	0.00026	0.00017	8.01516	—	0.00020	—	—	—	6.81031	8.01496	—	112.470
19.	5.50097	0.00017	0.00009	6.47393	—	0.00000	—	—	—	5.50089	6.47393	—	112.470

Average 112.471

CdCl₂ : 2Ag.

20.	6.11757	0.00004	+0.00003	—	9.56432	—	0.00013	0.00024	0.00147	6.11750	—	9.56590	112.470
21.	6.81040	0.00026	0.00017	—	10.64731	—	0.00010	0.00061	0.00136	6.81031	—	10.64918	112.471
22.	5.50097	0.00017	0.00009	—	8.59940	—	0.00008	0.00052	0.00190	5.50089	—	8.60174	112.469

Average 112.470

(a) Richards and Wells, Publications of the Carnegie Institution of Washington, No. 28, 1905; *Journ. Am. Chem. Soc.*, xxvii., 459.

phosphorus pentoxide. In the first place, the experiment of passing into water hydrobromic acid gas, formed as in our work by passing nitrogen through bromine and then through an emulsion of red phosphorus in concentrated hydrobromic acid solution, and dried first by fused calcium bromide and then by phosphorus pentoxide, was performed in this laboratory some years ago in connection with the analysis of cobalt and nickel bromides (Richards and Baxter, *Proc. Amer. Acad.*, 1899, xxxiv., 361). In this experiment no phosphorus could be discovered in the aqueous solution. In the second place, in two analyses of bromides which had been heated in hydrobromic acid gas, the filtrates from the silver bromide precipitates were evaporated to small bulk and tested for phosphoric acid, with negative results, while the slight residues obtained by filtering the aqueous solutions of the original bromides also showed in one case the complete absence of phosphorus, and in the other the presence of only a minute trace of this substance, although in the latter case the salt has been sublimed in a current of hydrobromic acid, and therefore contained maximum amounts of phosphorus (Baxter, *Proc. Amer. Acad.*, 1903, xxxix., 248). This result was to be expected from a consideration of the fact that the hydrobromic acid gas used in these experiments was diluted with at least twice its volume of nitrogen. In the light of this evidence it seems safe to assume that in the numerous analyses of bromides which have been carried out in this laboratory in recent years, no error was introduced by the use of phosphorus pentoxide as a drying agent for the hydrobromic acid gas. Nevertheless, with more concentrated hydrobromic acid, doubtless it would be unwise to use this drying agent.

It is interesting to compare the results of the analyses of the different fractions of material.

Fraction.			Average.
I.	CdCl ₂ : 2Ag	112.468	112.470
I.	CdCl ₂ : 2AgCl	112.471	
II., Series 1	CdCl ₂ : 2Ag	112.456	112.469
II., Series 1	CdCl ₂ : 2AgCl	112.481	
II., Series 2	CdCl ₂ : 2Ag	112.471	112.471
II., Series 2	CdCl ₂ : 2AgCl	112.470	
II.	CdBr ₂ : 2Ag	112.467	112.466
II.	CdBr ₂ : 2AgBr	112.465	
III.	CdBr ₂ : 2Ag	112.472	112.468
III.	CdBr ₂ : 2AgBr	112.464	
Average	..	112.469	112.469

The close agreement of the results from fraction II. by different methods and of the results from all three fractions leaves no doubt of the identity of the different specimens of material.

No matter how the results are averaged, the same conclusion is reached as in the preliminary paper, *i.e.*, that the atomic weight of cadmium lies very near the value 112.47 (Ag = 107.930).

It is interesting to compare the results of our work with those obtained by other experimenters. From the following list of investigations upon the atomic weight of cadmium it can be seen that this subject has attracted considerable attention, especially in recent years. The following atomic weights are assumed:—O = 16.00; C = 12.00; S = 32.06; Cl = 35.47; Br = 79.96; Ag = 107.93; I = 126.98:—

The greater portion of this list is to be found in Clarke's "Recalculation of the Atomic Weights," Smithsonian Mis. Coll., 1897.

Stromeyer (*Schweigger's Journ.*, 1818, xxii., 366).

Cd : CdO		111.5
Cd : CdS		113.8
Cd : Cl ₂		112.8
Cd : I ₂		111.7

von Hauer (*Journ. Prakt. Chem.*, 1857, lxxii., 350).

CdSO ₄ : CdS		111.94
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Lenssen (*Journ. Prakt. Chem.*, 1860, lxxix., 281).

CdC ₂ O ₄ : CdO		112.0
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Dumas (*Ann. Chem. Pharm.*, 1860, cxiii., 27).

CdCl ₂ : 2Ag		112.43
		111.95

Huntington (*Proc. Amer. Acad.*, 1881, xvii., 28).

CdBr ₂ : 2Ag		112.23
CdBr ₂ : 2AgBr		112.23

Partridge (*Amer. Journ. Sci.*, [3], 1890, xl., 377).

CdC ₂ O ₄ : CdO		111.80
CdSO ₄ : CdS		111.73
CdC ₂ O ₄ : CdS		111.67

Morse and Jones (*Amer. Chem. Journ.*, 1891, xiv., 261).

Cd : CdO		112.07
CdC ₂ O ₄ : CdO		112.02

Lorimer and Smith (*Zeit. Anorg. Chem.*, 1892, i., 364).

CdO : Cd 112.04

Bücher "Doctoral Dissertation," Baltimore, Md., 1895.

CdC₂O₄ : CdO 111.88

CdC₂O₄ : CdS 112.15

CdCl₂ : 2AgCl 112.37

CdBr₂ : 2AgBr 112.39

Cd : CdSO₄ 112.35

Cd : CdO (porcelain) 112.08

Cd : CdO (platinum) 111.89

Hardin (*Journ. Amer. Chem. Soc.*, 1896, xviii., 1016).

CdCl₂ : Cd 112.12

CdBr₂ : Cd 112.06

Cd : Ag 111.99

Morse and Arbuckle (*Amer. Chem. Journ.*, 1898, xx., 536).

Cd : CdO 112.38

Baxter and Hines (*Journ. Amer. Chem. Soc.*, 1905, xxvii., 222).

CdCl₂ : 2Ag 112.462

CdCl₂ : 2AgCl 112.476

The relative value of many of these determinations has already been several times discussed, and since it is invariably a difficult matter intelligently to criticise experimental work without an actual repetition of the experiments, for frequently some constant source of error is so securely hidden that it may be detected only by the most careful investigation, no attempt at criticism is made here. (Clarke, Partridge, Morse and Jones, *loc. cit.*; Richards, *Amer. Chem. Journ.*, 1898, xx., 547.)

Furthermore, the uncertainty which now exists as to the relation between several fundamental atomic weights, *e.g.*, silver and oxygen, makes it a matter of considerable doubt whether, when this uncertainty is removed, some of the discrepancies in the foregoing table will not disappear. (Richards, Publications of the Carnegie Institution, No. 28, p. 67; "Report of the International Committee on Atomic Weights," *Journ. Am. Chem. Soc.*, 1906, xxviii., 1).

Attention should be called to the agreement with ours of the results of Bücher's painstaking work upon the halogen compounds of cadmium. The values from cadmium chloride vary between 112.26 and 112.46, with an average of 112.37, but if the first seven of his twenty-one experiments are rejected, his average becomes 112.40, and six of his results are as high as 112.43. His analyses of the bromide vary between 112.30 and 112.46, with an average of 112.39.

The results of this investigation are then as follows:—

1. The value for the atomic weight of cadmium previously found by analysis of cadmium chloride, 112.47 (Ag = 107.930), is supported by the analysis of cadmium bromide and by new analyses of cadmium chloride.

2. Phosphorus pentoxide is found to be attacked by pure hydrochloric acid gas, and hence is unsuited for drying this gas, thus confirming the results of Bailey and Fowler.

3. It is shown that no appreciable error is introduced from this source, if a dry salt is fused in a current of hydrochloric acid which has been dried by phosphorus pentoxide.

4. It is pointed out that in the case of hydrobromic acid diluted with twice its volume of nitrogen no similar effect is produced.

We are deeply indebted to the Carnegie Institution of Washington, with whose generous aid this investigation has been completed, and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 1st, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

(Concluded from p. 240).

192. "Some Derivatives of Catechol, Pyrogallol, Benzo-phenone, and of Substances Allied to the Natural Colouring Matters." By WILLIAM HENRY PERKIN, jun., and CARL WEIZMANN.

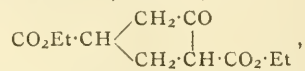
This communication contains the description of the preparation and properties of a number of new substances obtained at different times in connection with researches on the constitution of brazilin, hæmatoxylin, and other natural colouring matters.

193. "Experiments on the Synthesis of the Terpenes. Part IX. The Preparation of Cyclopentanone-3-carboxylic Acid and of Cyclohexanone-4-carboxylic Acid (δ -Keto-hexahydrobenzoic Acid)." By FRANCIS WILLIAM KAY and WILLIAM HENRY PERKIN, jun.

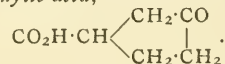
When ethyl butane- $\alpha\beta\delta$ -tricarboxylate,—



is heated with sodium, and the product acidified, it yields ethyl cyclopentanone-2 : 4-dicarboxylate,—

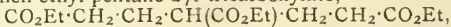


a colourless oil, which distils at 166° (18 m.m.), and, when digested with dilute sulphuric acid, is readily hydrolysed with elimination of carbon dioxide and formation of cyclopentanone-3-carboxylic acid,—

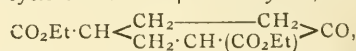


This new acid melts at 65°, and yields an oxime (m. p. 141°) and a semicarbazone (m. p. 195°).

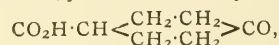
When ethyl pentane- $\alpha\gamma\epsilon$ -tricarboxylate,—



is treated with sodium, it is converted in a similar manner into ethyl cyclohexanone-2 : 4-dicarboxylate,—



which distils at 180° (20 m.m.), and, on hydrolysing with dilute sulphuric acid, yields δ -keto-hexahydrobenzoic acid,—



this method of preparation being much more convenient than that previously described (*Trans.*, 1904, lxxxv., 418). The authors wish to reserve the further investigation of the substances described in this preliminary communication.

194. "The Hydrolysis of 'Nitrocellulose' and 'Nitroglycerin.'" By OSWALD SILBERRAD and ROBERT CROSBIE FARMER.

The authors have studied the hydrolysis of nitrocellulose, nitroglycerin, and mixtures of the two in the form of cordite and ballistite. The hydrolysis is complicated by the simultaneous reduction of the nitric acid, as shown by (1) the formation of large quantities of nitrites, (2) the degradation of the cellulose and glycerol to hydroxy-acids, &c., (3) the abnormally high saponification equivalents found (9.2 to 9.5 for pentanitrocellulose and 4.85 for nitroglycerin), (4) the abnormality of the velocity curves. Intermediate products are formed which are gradually acted on by the alkali; these are practically insoluble in water, and do not give rise to free acid when left in contact with water for several days.

With the aid of velocity determinations with varying quantities of gun-cotton, a formula was deduced whereby

the velocity was calculated with which the reaction would occur if perfect diffusion took place. The following results were obtained when gun-cotton was suspended in 400 c.c. of acid or alkali at 37°8'.

Grms. of gun-cotton.	Concentration of H or OH ions.	Velocity (grm.-equiv. of acid liberated per hour).	
		Calculated.	Found.
1. <i>Hydrolysis by Baryta Solution.</i>			
3'10	0'197	0'0035	0'0033
4'97	0'191	0'0051	0'0053
20'42	0'096	0'0070	0'0071
22'10	0'189	0'0144	0'0142
∞	1'000	0'168	—
2. <i>Hydrolysis by Nitric Acid.</i>			
5'10	0'821	0'00018	0'00018
10'00	0'821	0'00022	0'00021
20'35	0'821	0'00025	0'00024
∞	1'000	0'000347	—

From the limiting velocities thus determined, it was calculated that the hydrolysis of nitrocellulose will take place with the minimum velocity when the concentration of the hydrogen ions is 3.7×10^{-6} and that of the hydroxyl ions 7.8×10^{-6} grm.-equivalent per litre. Under these conditions, the hydrolysis will proceed with such a velocity as to liberate 5.6×10^{-6} grm.-equivalents of acid per litre of water per year.

195. "The Acidic Constants of some Ureides and Uric Acid Derivatives." By JOHN KERFOOT WOOD.

The investigation was undertaken with the object of determining the influence of other groups on the acidity of the imino-group. In compounds which contain the grouping $\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}$, there appears to be a mutual reinforcement of the imino-groups, analogous to the reinforcement of the carboxyl groups in succinic acid. Divergent results were obtained with barbituric and C-ethylbarbituric acids, the dissociation constants of which are many times greater than those of the other substances investigated; this high acidity is due to the CH_2 or $\text{CH}(\text{C}_2\text{H}_5)$ group.

196. "The Affinity Constants of Xanthine and its Methyl Derivatives." By JOHN KERFOOT WOOD.

The author described the results of determinations of the basic and acidic constants of xanthine, 7-methylxanthine, the three isomeric dimethylxanthines, and caffeine. There is no great variation in the values of the basic constants, but a very striking difference in the values of the acidic constants is to be noticed. The dimethylxanthines, especially paraxanthine and theophylline, are stronger acids than any of the other members of the series. Moreover, when the results for the three dimethylxanthines are compared amongst themselves, it is seen that they are not in agreement with the constitutions of the isomerides. The conclusion is drawn that these results are to be explained by a stereochemical influence exerted by the two methyl groups, the influence varying in magnitude according to the positions in the xanthine nucleus which the methyl groups occupy.

197. "The Explosive Combustion of Hydrocarbons." (II.). By WILLIAM ARTHUR BONE, JULIAN DRUGMAN, and GEORGE WILLIAM ANDREW.

The authors have further examined the phenomena associated with the "inflammation" of mixtures of ethane or ethylene and oxygen corresponding to $\text{C}_2\text{H}_6 + \text{O}_2$ and $3\text{C}_2\text{H}_4 + 2\text{O}_2$ respectively, by a method which allows of discrimination between the various products according as they arise at an earlier or later stage in the flame. In each case, steam, aldehydes, ethylene, and acetylene are prominent during the initial stages of combustion, whilst carbon is a later product. Steam is so rapidly decomposed by carbon at high temperatures that prolonged duration of the flame diminishes the quantity of water which separates on cooling.

The authors have also succeeded in producing "detonation" in mixtures of ethane, or butane, and oxygen corresponding to $\text{C}_2\text{H}_6 + \text{O}_2$ and $\text{C}_4\text{H}_{10} + 2\text{O}_2$ respectively, at initial pressures of 900 m.m. and upwards. The mechanism of combustion under these conditions does not, however, appear to be essentially different from what it is in ordinary flames.

198. "Contributions to the Theory of Solutions. I. The Nature of the Molecular Arrangement in Aqueous Mixtures of the Lower Alcohols and Acids of the Paraffin Series. II. Molecular Complexity in the Liquid State. III. Theory of the Intermiscibility of Liquids." By JOHN HOLMES.

The author has determined the relative densities of mixtures of carbon disulphide with ethyl- and *n*-propyl-alcohols respectively, and of pyridine with water and ethyl alcohol.

From a consideration of the nature of the volumetric changes occurring in these and other mixtures of liquids, it is concluded that the sphere of activity of a molecule is not an invariable function of the molecular volume, as ascertained from its molecular weight and specific gravity.

On these changes the author bases a theory of intermiscibility, depending on differences in the degree of repulsion between liquid molecules.

199. "The Relation between Natural and Synthetical Glycerolphosphoric Acids." (Part II.). By FRANK TUTIN and ARCHIE CECIL OSBORN HANN.

With the object of ascertaining the nature of the natural and synthetical glycerolphosphoric acids, the authors have synthesised the unsymmetrical or α -acid, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{PO}_3\text{H}_2$, and the symmetrical or β -acid, $(\text{CH}_2\cdot\text{OH})_2\cdot\text{CH}\cdot\text{O}\cdot\text{PO}_3\text{H}_2$, and have compared the barium and brucine salts with the corresponding salts of the natural and synthetical acids.

α -Glycerolphosphoric acid was prepared by the action of phosphoric acid on β -dichlorohydrin and subsequent hydrolysis of the product.

β -Glycerolphosphoric acid was prepared by the hydrolysis of β -diglycerolphosphoric acid (m. p. of calcium salt 249—250°), which had been obtained by the action of phosphoryl chloride on α -dichlorohydrin and subsequent hydrolysis of the product.

The racemised natural acid was prepared by the hydrolysis of egg lecithin with hot baryta solution.

The synthetical acid was obtained from glycerol and phosphoric acid under such conditions as had been previously shown to give only the mono-ester.

The barium salts of these acids differ considerably in appearance, solubility, and in the amount of water they contain. The brucine salts differ in the amount of their water of crystallisation, but all melt at 157—159°, and not at 181°, as stated by Carré (*Comptes Rendus*, 1903, cxxvii., 1070).

It is concluded from the results of this investigation that the natural and synthetical glycerolphosphoric acids are differently constituted mixtures of the α - and β -acids.

200. "Thiocarbonic Acid and some of its Salts." By IDA GUENEVERE O'DONOGHUE and ZELDA KAHAN.

Thiocarbonic acid has been prepared by the cautious addition of calcium thiocarbonate to cold concentrated hydrochloric acid. It is a heavy, red oil, boiling with decomposition at 50°, and on distillation under diminished pressure decomposes into carbon disulphide, hydrogen sulphide, and sulphur. Thiocarbonic acid expels carbon dioxide from carbonates, and on treatment with metallic sodium or potassium yields the corresponding salts. The normal metallic thiocarbonates are formed by the action of the salts of weak acids on thiocarbonic acid, and are constituted similarly to the corresponding carbonates. The acid has therefore the formula H_2CS_3 . The salts are very unstable both in air and in a vacuum, some decompose quantitatively into carbon disulphide and metallic sulphide, whilst others give, under similar conditions, a variety of basic compounds.

201. "Studies in Optical Superposition." (Part II.). By THOMAS STEWART PATTERSON and JOHN KAYE.

Di-*l*-menthyl-*l*-tartrate, di-*l*-menthyl diacetyl-*l*-tartrate, and sodium *l*-menthyl *l*-tartrate have been prepared and examined in regard to their optical activity, both in the homogeneous condition, so far as possible, and also in solution. The results are discussed in connection with the problem of optical superposition.

202. "Optically Active Dihydrophthalic Acid." By ALLEN NEVILLE.

When the hydrogen strychnine salt of trans- $\Delta^3:5$ -dihydrophthalic acid is fractionally crystallised from alcohol, the acid is resolved into its *lævo*- and *dextro*-isomerides. These melt at 122° and do not lose weight at 100° . They are readily soluble in alcohol, fairly so in ether or chloroform, and insoluble in water. They have $[\alpha]_D$ about 126° in alcohol and about 140° in chloroform.

Heated with water or alkali, they pass to the optically inactive $\Delta^2:6$ -modification, and, warmed with acetic anhydride, are transformed to the *cis*- $\Delta^3:5$ -modification of dihydrophthalic acid.

ERRATA.—P. 230, col. 2, line 21, for "disulphide" read "ethyl sodium thiosulphate." Line 22, for "the mercaptan" read "some mercaptan." Line 24, for "cm." read "dcm."

PHYSICAL SOCIETY.

Ordinary Meeting, November 9th, 1906.

Prof J. PERRY, F.R.S., President, in the Chair.

MR. G. F. C. SEARLE gave an Exhibition and Description of Apparatus for Students' Practical Work in Physics.

1. *Diagram of Forces*.—The student finds the magnitude and line of action of the resultant of a number of co-planar forces, represented by lines on a diagram: (a) by the parallelogram law; (b) by the methods of analytical statics.

2. *The Ballistic Balance*.—Two spheres are suspended by bifilar suspensions. The smaller sphere is released from an electromagnet. The highest points reached by the spheres after impact are observed. The student determines the ratio of the masses and the coefficient of restitution.

3. *Harmonic Motion of a Rigid Body*.—An inertia bar is suspended by a torsion-wire. The couple for a radian is deduced from observations of angles due to known couples. Couples are produced by threads round a cylinder attached to the wire, the threads passing over ball-bearing pulleys and carrying masses. The angles are observed by a simple goniometer. The calculated and observed times are compared.

4. *Determination of the Radius of Curvature of a Concave Mirror by the Oscillation of a Sphere*.—If T be the time of oscillation of the sphere, R the radius of the mirror, and r the radius of the sphere $T = 2\pi \sqrt{7(R-r)/5g}$.

5. *Comparison of Moments of Inertia*.—Two inertia bars A and B are joined by a wire. If T_1 be the time of vibration when B is fixed and A performs torsional vibrations, and T_2 be the time when A is fixed and B vibrates, then $K_1 T_2^2 = K_2 T_1^2$ where K_1 , K_2 are the moments of inertia of A and B. If the system is hung up by a silk thread and A and B move in opposite directions, the periodic time T_3 is given by $1/T_3^2 = 1/T_1^2 + 1/T_2^2$. A pointer attached to the wire at the "centre of gravity" of the moments of inertia does not vibrate.

6. *System with Two Degrees of Freedom*.—Two inertia bars are connected by a wire and the system is suspended by a wire. There are two normal modes of vibration. In one the bars move in the same direction, in the other they move in opposite directions. The times observed for the two normal vibrations are compared with the times deduced from those observed when each bar vibrates alone.

7. *Determination of the Critical Acceleration of a Pedometer*.—In a pedometer a weight is supported by a spring which is strong enough to sustain it when the instrument is at rest. If the pedometer have an upward acceleration exceeding f the spring cannot sustain the weight, and the motion of the weight starts the mechanism. The pedometer is attached to a spring vibrating vertically. If T be the time of vibration and a the amplitude, the maximum upward acceleration is $4\pi^2 a/T^2$. If the mechanism just works $f = 4\pi^2 a/T^2$.

8. *Determination of the Roots of Bessel's Function of Zero Order by means of a Vibrating Chain*.—A chain is suspended at one end. By properly timed impulses, applied near the top of the chain, it can be made to vibrate with one, two, three . . . nodes. If the length of the chain be l and the length of the equivalent pendulum for any mode of vibration be λ , then $J_0\{2\sqrt{l/\lambda}\} = 0$. The student finds the time of vibration for each mode, and compares it with that given by the theory (Tait, "Dynamics," p. 287).

9. *Apparatus for Testing Hooke's Law*.—Two wires hung side by side carry a jointed frame holding a spirit level. When the load on one wire is increased the level is brought back to its zero reading by a micrometer-screw working in one side of the frame. By taking cycles of loading and unloading, hysteresis effects can be observed in copper wire (*Proc. Camb. Phil. Soc.*, 1900).

10. *Determination of Young's Modulus and Rigidity for a Wire*.—Two inertia bars are connected by the wire. The system is suspended by threads attached to the bars so that the bars and the wire are horizontal. If T_1 be the time of vibration of the bars in the horizontal position, $T_2^2 = 8\pi Kl/Ea^4$. One bar is now fixed so that the wire is vertical. If T_2 be the time of torsional vibrations of the other bar, $T_2^2 = 8\pi Kl/na^4$. Hence, $E/n = T_2^2/T_1^2$, where E = Young's modulus, n = simple rigidity, K = moment of inertia of bar, l = length of wire, and a = radius of wire (*Phil. Mag.*, Feb., 1900).

11. *Determination of Coefficient of Restitution*.—A steel bicycle ball is allowed to fall from an electromagnet on to a steel anvil. If the ball falls through h and rises through h' , the coefficient of restitution (e) is given by $e = \sqrt{h'/h}$. The student also finds the loss of energy and the change of momentum which occur on impact.

12. *Apparatus for Experiments on Common String*.—When a mass, M , is suspended by a piece of common twisted (not plaited) string, the string exerts a couple G upon the mass. If the mass be allowed to start from rest and if it make n revolutions in time t , $G = 4\pi n K/t^2$, where K is the moment of inertia of the mass. It is found that G is proportional to M .

13. *Resonance Experiments with a Bottle*.—If the air in a bottle resounds to a fork of frequency n when the volume of air is S , then $S = Cv^2/n^2$, where v is the velocity of sound and C is a constant. Resonance is obtained for a series of forks, the volume S being adjusted by water. On plotting S against $1/n^2$ a straight line is obtained. This line cuts the axis of S at a point which indicates the "correction" due to the neck of the bottle.

14. *Resonator with "Thin Plate" Opening*.—A jar is fitted with a flat top pierced by a rectangular opening. The area of the opening is varied by a sliding plate. The volume of the air in the jar is varied by water. If the opening be circular, and if n be the frequency and v the velocity of sound,—

$$n = [v \times (\text{area of opening})^{\frac{1}{2}}] / [2\pi^{\frac{1}{2}} (\text{volume of resonator})^{\frac{1}{2}}]$$
This formula is nearly true for openings of any form.

15. *Mechanical Equivalent of Heat*.—Heat is produced by friction between two cones. The outer cone revolves and the inner one is prevented from revolving by a string passing round a wheel attached to the cone and supporting a weight (E. H. Griffiths, "Thermal Measurement of Energy," p. 125).

16. *Determination of Thermal Conductivity of Copper*.—(*Phil. Mag.*, Jan., 1905).

17. *Determination of Thermal Conductivity of India-rubber.*—Steam passes through a rubber tube. Part of the tube is immersed in water in a calorimeter. If M be the water equivalent of the calorimeter and its contents, K the thermal conductivity of rubber, a and b the external and internal radii of the tube, l the length immersed, and θ the temperature of the calorimeter,—

$$K = \frac{M}{2\pi l(100 - \theta)} \cdot \frac{d\theta}{dt} \cdot \log_e \left(\frac{a}{b} \right).$$

18. *Comparison of Refractive Indices.*—A double convex lens is placed in contact with a horizontal mirror; its focal length is f . When a little water (μ_1) is placed between the lens and the mirror, the focal length of the system becomes F_1 . When aniline (μ_2) is substituted the focal length is F_2 . Then $(\mu_2 - 1)/(\mu_1 - 1) = [(F_2 - f) \cdot F_1]/[(F_1 - f) F_2]$. The focal length is found by making a pin coincide with its image.

19. *Focal Length of a Compound Lens System.*—Light from a distant object passes through the system. The system is adjusted on a revolving table so that the Nodal Point of emergence lies on the axis of revolution. In this case the image does not move when the table is slightly turned. The focal length is then equal to the distance from the axis of revolution to the ground-glass or pin by which the position of the image is marked.

20. *Focal Lines by Reflection at a Concave Mirror.*—A piece of ground-glass, with horizontal and vertical cross lines, is illuminated by a flame. Pins are placed to mark the positions of the images of the vertical and of the horizontal lines formed by the mirror, whose axis is horizontal. If the distances of the cross lines and of the images of the vertical and horizontal lines from the mirror be u, v_1 , and v_2 , then $2/r \cos i = 1/u + 1/v_1$, $2 \cos i/r = 1/u + 1/v_2$, where r is the radius of the mirror and i is the angle of incidence.

21. *Experiments with an Astigmatic Lens.*—Light from a pin-hole passes through the lens and falls on a ground-glass screen. One face of the lens is spherical, the other cylindrical, and the lens is fitted into a plate with a circular opening. When u is the distance of the pin-hole from the lens, focal lines are formed at distances v_1 and v_2 , and the circle of least confusion at w from the lens. Then $1/u + 1/v_1 = 1/f_1$, $1/u + 1/v_2 = 1/f_2$, and $1/u + 1/w = \frac{1}{2}(1/f_1 + 1/f_2)$, where f_1, f_2 are the focal lengths in the principal planes of the lens.

22. *Curvature of the Field of a Lens.*—Light from a white back-ground marked by black cross lines passes obliquely through a lens. By aid of a pair of cross wires the images of the vertical and horizontal cross lines are found. These images lie on two curved surfaces. When the obliquity is small the surfaces are ellipsoids of revolution having the centre of the lens for one focus.

23. *Experiment on Spherical Aberration.*—Sodium light passes through a pin-hole and falls on a large lens. After passing the lens it falls on a ground-glass screen on which a scale is marked. By this scale the diameter of the luminous patch on the screen is measured for a series of positions of the screen. The position of the geometrical focus is found by "stopping down" the lens by a diaphragm with a small aperture. A clear glass scale lightly coated with paraffin-wax forms a good screen.

24. *Coulomb's Sine Experiment.*—To show that the couple on a magnet in a uniform magnetic field is proportional to the sine of the angle between the axis of the magnet and the direction of the field. The couple is measured by the torsion of a wire.

25. *Coulomb's Vibration Experiment.*—The vibration magnetometer employed has a long periodic time and small damping. It is practically a plumb-bob carrying a small magnet. The student compares the magnetic force at various distances from the pole of a Robison ball-ended magnet with the earth's magnetic force, and deduces the pole-strength of the Robison magnet. Ball-ended magnets have practically "true poles" (*Proc. Camb. Phil. Soc.*, 1902).

26. *Ball-ended Magnetometer.*—A Robison ball-ended magnet A B is supported on a pivot close to a drawing board. A second Robison magnet C D rests on the board, and deflects A B. If m be the pole-strength of C D the resultant moment of the four forces m/AC^2 , m/AD^2 , m/BC^2 , and m/BD^2 about the pivot is equal to $H \sin \theta$, where H = Earth's force, l = length of pivotted magnet, and θ = deflection. Hence m is found.

27. *Comparison of 10 Ohms with 1 Ohm.*—A coil X of nearly 10 ohms is to be compared with a standard coil U of 1 ohm. By thick copper connectors three coils, each nearly equal to 3U, can be arranged in parallel, when the resistance is P, or in series, when the resistance is S. Then to the second order $S = 9P$. P is first compared with U. Then U is put in series with S and X is compared with the whole (*Glazebrook, Phil. Mag.*, 1900).

FARADAY SOCIETY.

Ordinary Meeting, November 13th, 1906.

Dr. F. MOLLWO PERKIN, Treasurer, in the Chair.

MR. W. POLLARD DIGBY read a paper entitled "*Some Investigations relative to the Depreciation of Electrolytically Produced Solutions of Sodium Hypochlorite.*"

This deals in the first place with depreciation taking place in bottles of various colours in which dark amber bottles gave the best results, the loss in 1817 days being about 40 per cent for a solution containing 4.216 grms. of available chlorine per litre. The corrosive action of hypochlorite solutions upon various metals is then discussed, and the depreciations due to graphite, copper, zinc, lead, and iron plates immersed in such solutions are set forth for a period of 480 hours. A much greater depreciation takes place, due to galvanic action, when two dissimilar metals immersed in the liquid are connected by an insulated wire; the paper gives records in the case of twenty-one different couples. When iron is present as one metal in such a couple, the depreciations are generally greater than for any two other metals.

As regards the area of the exposed surface in the cases of single metals immersed in hypochlorite solutions, it was found that doubling or trebling the surface doubled or trebled the rate of depreciation.

Brief reference is made to the value of protective coatings as applied to metal-couples, but no conclusive results were obtained.

As it is a matter of difficulty to paint evenly the inside of small plates, and, still more, of pipes, the writer deprecates reliance upon insulating materials for the protection of any vessel in which hypochlorite liquids are stored, or of any metallic piping in contact with hypochlorite liquids. When once the paint breaks down, corrosion of the metal will follow at a rapid rate.

Accounts are also given of the value of bitumen as a protective agent for wood exposed to hypochlorite solutions.

In conclusion the author urges that storage, transport, and methods of conveyance from place to place, or even from one part of a factory to another, are details meriting attention. Certain conditions of storage may clearly be regarded as fatal to stability, particularly those in which the galvanic action of dissimilar metals is likely to arise.

MR. CHAS. V. BIGGS then read his paper describing "*The Hermite Electrolytic Process at Poplar.*"

This paper is a contribution to the data at present available on the subject of the electrolytic productions of hypochlorites. It consists of a description of the plant in use at Poplar for the preparation of a solution containing about 4.5 grms. of available chlorine per litre, for use as a disinfectant in the borough.

The system adopted is to mix a certain quantity of fluid in an elevated tank, and then to allow this fluid to flow through four double troughs or cells, placed one above the other so that the liquid descends continuously by gravity.

Each trough is divided laterally by a partition, and in each of the two divisions five distinct "elements" are suspended. The positive plates are of thin platinum-wire wound upon slate-slabs, and the negative plates are of zinc. There are thus four troughs each containing ten "elements," or forty cells in all. After passing through the successive cells, the liquid discharges into a carboy. Sodium hydroxide is used as a preservative; it flows drop by drop into the carboy as it is filling, and serves to neutralise free hypochlorous acid. As the liquid passes through the troughs it is subjected to the action of a current of 15 amperes at 230 volts, being 5.6 volts per cell.

The tank is charged by placing in it 100 litres of a saturated solution of sodium chloride and 20 litres of a saturated solution of magnesium chloride. To this is added as much water as will bring the whole up to 840 litres. The rate of flow through the apparatus is 3½ pints per minute.

Curves are appended showing (1) the rise in value of the solution as it passes through the cells, amounting to about 1 gm. per litre for 10 cells; (2) efficiency in grms. per B.T.U. for this plant, which is highest at a current of 16 amperes. Above this ampère energy is wasted in heat, and below it the flow becomes too high.

A number of tests of samples of the liquid made are given. Liquid made during the warm weather of the exceptional summer of 1906, at a temperature of 104° F., was found to have lost only 0.1 gm. available chlorine per litre in six weeks. Several samples of liquid made before the conditions of the plant (as to mixing, rate of flow, &c.) were very fully determined, showed losses of 0.1 and 0.2 gm. per litre in six months; the higher strengths (4.8 to 5.3 grms. per litre) losing 0.5 gm in six months.

The author concludes that the magnesium hypochlorite, as made at Poplar, is sufficiently stable for practical purposes, and that it could be made in a warm climate without necessarily rapid deterioration. The warm weather specimens quoted had been kept in ordinary dark glass bottles, merely corked.

Mr. J. B. C. KERSHAW (communicated) considered that electrolytic hypochlorite was unlikely to replace bleaching-powder at present prices. He criticised the efficiency of the Hermite plant at Poplar.

Dr. R. S. HUTTON hoped that further information regarding the electrodes and other important details of the Poplar plant, and also further data regarding cost and efficiency, would be forthcoming. He drew attention to the theoretical work that had been done on the Continent. Replying to Mr. Kershaw's strictures, efficiency depended on concentration. At Poplar high concentrations were used, so the efficiency was relatively low.

Dr. F. W. ALEXANDER gave complete details regarding the cost of running the Poplar plant. The plant has been producing an average of 200 gallons a day of 0.4 gm. solution since January last at a total cost for current and material of under £33. Two labourers sufficed to watch the plant and bottle the solution. The defects of the original Hermite process had been successfully overcome. They had no trouble with non-conducting films on the zinc cathodes. Non-stability was caused by the presence of undecomposed salt in solution.

Dr. S. RIDEAL was of opinion that the convenience of being able to make hypochlorite on the spot as required for disinfecting purposes rendered it far more suitable than bleaching-powder. The dust nuisance caused by motors rendered the use of a sterilising fluid for street watering a necessity.

Mr. L. A. SMART remarked on the value of such electro-chemical processes to borough engineers if they could be arranged to run so as to increase the load factor of the power station.

Mr. W. DEFRIES pointed out that although the price of raw materials would probably not decrease, that of power tended to diminish, so electrolytic hypochlorite would in

time compete favourably, even as regards price, with chloride of lime.

The authors' replies were reserved for the *Transactions*.

The paper by Dr. ALEX. C. C. CUMMING "*On the Electro-chemistry of Lead*" was taken as read, and the discussion postponed until the December meeting.

NOTICES OF BOOKS.

Soldering, Brazing, and the Joining of Metals. By THOMAS BOLAS, F.C.S., F.I.C. Third Edition. London: Dawbarn and Ward, Ltd. 1906.

OCCASIONS arise in every laboratory when the power to successfully braze or solder metal-work is of great value. Little accidents happen to apparatus while in use that must be instantly set right; opportunity occurs for some device in metal, too trivial to hand over to a professional metal worker, which if it could be carried out at the moment would help one over a difficulty.

This little book gives plain instructions and practical hints on soldering and metal working, from the simple operations of putting a patch on a water-bath or joining a lead pipe to the building up of elaborate designs in art metal-work, and is well worth the modest sixpence at which it is published.

Elementary Science of Common Life (Chemistry). By W. T. BOONE, B.A., B.Sc. London: University Tutorial Press, Ltd. 1906.

THIS book has been written to meet the requirements of the Syllabus for Subject XXVI. of the Board of Education Examinations, and candidates cannot do better than to use it, while other students also will find it stimulating and helpful. It gives directions for an instructive course of experimental work, which can be performed with a limited amount of comparatively simple apparatus, beginning with six chapters on physics, more especially heat, and proceeding to the chemistry of air, fuels, water, and various chemical substances, such as the common acids, bases, metals, and salts. The practical usefulness in every-day life of the information imparted is kept well before the students' eyes, so that the interest of the boy of average intelligence is certain to be aroused, and in spite of the fact that he is preparing for an examination he should acquire a certain approximation to the valuable scientific habit of thought which it should be the aim of the teacher to produce at all costs. The book contains the examination papers set by the Board in 1905, besides sets of questions, and the author is to be congratulated on the skill with which he handles his subject.

J. G. Gentile's Lehrbuch der Farbenfabrikation. ("J. G. Gentile's Text-book of the Manufacture of Colours"). Third Edition. Edited by Dr. A. BUNTROCK. Volume I. Braunschweig: Friedrich Vieweg und Sohn. 1906.

THE third edition of Gentile's Text-book of the Manufacture of Colours will be welcomed by chemists and others interested in the industry who have found the original, which is now somewhat out of date, useful. In the first volume, which is devoted to the earthy pigments, naturally the chief alterations relate to the improvements of mechanical appliances, and it gives general methods of obtaining and purifying the pigments and preparing them for use. The second part of the book enumerates all the commonly used earthy colouring materials, describes the application of general methods to particular cases, and also discusses the properties and uses of the individual substances, notes on the analysis of the raw materials being included. The book will be of interest to chemists and manufacturers, and also to those who use the pigments and who wish to acquire some knowledge of their composition and properties.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 18, October 29, 1906.

Dissociation of Matter under the Influence of Light and Heat.—Gustave Le Bon.—The author describes an experiment which gives a further proof of the universal radio-activity of matter—a fact which he has been trying to demonstrate for some years. All bodies possess to a very slight degree the properties which radium and uranium have in a very high degree. It is not only under the influence of heat that metals tend to lose their faculty of radio-active emission; they lose it also to a slight degree when under the influence of prolonged action of light, even when the luminous source does not sensibly raise their temperature. A metal which gives an almost instantaneous discharge at first, and an electrometer when luminous rays first fall on its surface, loses the residue more and more slowly. Ramsay and Spencer have investigated this "fatigue of metals" under the influence of light. They attribute it to a modification of equilibrium of the atomic elements of its surface by reason of the loss of a certain number of electrons produced by the disintegration of the material.

Phenylic Migration. Method of Fixation of Hypoiodous Acid and Elimination of Hydriodic Acid.—M. Tiffeneau.—During the fixation of the radicle IOH the oxyhydrile shows a preference for the most substituted carbon atom and the one nearest to the phenyl. When the HI is eliminated the oxyhydrile nearest to the phenyl remains unattacked, and migration of the phenyl takes place. On the contrary, when the oxyhydrile is furthest away from the phenyl the elimination of the HI tends to form ethylene oxides.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxix., No. 13, 1906.

Oxides of Sulphuretted Hydrogen.—Emil Fromm and José de Seixas Palma.—Sulphurous acid (H_2SO_3) is the mother substance of the sulphonic acids $\text{R}.\text{SO}_3\text{H}$. H_2SO_2 (sulphoxylic acid), has not yet been prepared in the pure state, nor its salts, but hydrosulphites, e.g., $\text{Na}_2\text{S}_2\text{O}_4$, and sulphinic acids, $\text{R}.\text{SO}_2\text{H}$, sulphones, $\text{R}.\text{SO}_2.\text{R}$, and compounds of sulphonylic acid with aldehydes and ketones, are known. H_2SO , which may be called sulphur hydrate, is unknown, but substituted organic derivatives of it, e.g., the sulfoxides, $\text{R}.\text{SO}.\text{R}$, have been prepared. The authors have used benzyl chloride and alkali as reagents for the preparation of these oxides. Just as sulphurous acid is converted by their action until benzyl sulphonic acid, so sulphonylic acid can be converted into sulphinic acids and sulphones, and sulphur hydrate into sulfoxides, $\text{R}.\text{SO}.\text{R}$. When the action of these reagents on sodium hydrosulphite was investigated, it was found that a hot alkaline solution of the hydrosulphite behaved like a solution of sulphurous acid and sulphonylic acid salt. The sulphite gives with benzyl chloride sulphonic acid salt, and the sulphonylate gives benzyl sulphone. It must be assumed that sodium sulphonylate with benzyl chloride gives first benzyl sulphinic acid and then the further action of benzyl chloride gives benzyl sulphone. These experiments show that not only is sulphurous acid the mother substance of the sulphonic acids, but also sulphonylic acid, H_2SO_2 , is the mother substance of the sulphinic acids and sulphones.

Ammonium Syngenite.—J. D'Ans.—If gypsum is introduced into an almost saturated solution of ammonium sulphate and the whole allowed to stand at the ordinary temperature under a bell glass, the double salt is formed in a few days. It consists of glittering needles like potassium

syngenite. The author's experiments show that it contains only one molecule of water having the formula $(\text{NH}_4)_2\text{Ca}(\text{SO}_4)_2.\text{H}_2\text{O}$. It is stable at 25° .

New Nickel Reaction.—Hermann Grossmann and Bernhard Schück.—If a solution of dicyandiamide (which can be bought very cheaply) is boiled with a few drops of hydrochloric acid for a minute, then a nickel salt solution added and some caustic potash, a yellow crystalline precipitate is formed. This precipitate, which becomes flesh-coloured on heating, is very difficultly soluble in water and practically insoluble in ammonia. Caustic potash does not decompose it, even on boiling, but potassium cyanide at once dissolves it. Its formula is $\text{Ni}(\text{N}_4\text{H}_5\text{C}_2\text{O})_2 + 2\text{H}_2\text{O}$. The following table shows the sensitiveness of the test. Solution I. contains 1 gm. of nickel carbonate dissolved in a little hydrochloric acid, solution made up to 100 c.c. with water. Solution II. is a 5 per cent solution of dicyandiamide. In the second series of experiments Solution I. contains 1 gm. of nickel carbonate in 200 c.c. of water. Thus the test is not so delicate as that recommended by Tschugaeff, but the reagent is cheap and easily procurable. The test is not affected by the presence of cobalt, which gives no corresponding cobalt compound.

I. C.c.	II. C.c.	Total vol. C.c.	Remarks
10	10	45	Immediate yellow coloration and precipitate.
5	10	25	
2	5	20	Intense coloration. Precipitate on boiling.
1	5	20	
5	10	50	Immediate yellow coloration and precipitate.
2	10	40	Precipitate on boiling.
1	8	40	Light coloration. Precipitate after some minutes.
0.5	5	20	Precipitate on standing for one hour.
0.2	5	20	Very faint yellow coloration. Precipitate after two days.

Quantitative Separation of Beryllium from Aluminium.—B. Glassmann.—The author's method is based upon the fact that when sodium thiosulphate is added to a solution of a beryllium salt and the liquid is boiled, it becomes turbid in consequence of the sulphur separated, but the beryllium remains in solution as sulphite or basic sulphite, while the aluminium is precipitated quantitatively as hydroxide. The solution of the oxides containing hydrochloric or sulphuric acid is first approximately neutralised with sodium carbonate, an excess of sodium thiosulphate is added, and the whole boiled till the smell of sulphurous acid has passed off. The liquid is then heated for half-an-hour on the water-bath. The aluminium oxide mixed with sulphur is washed and ignited. In the filtrate the excess of thiosulphate is decomposed with hydrochloric acid, and the beryllium is precipitated with ammonia (or better with an iodide-iodate mixture as described in the following article).

Quantitative Determination of Beryllium.—B. Glassmann.—Iodine is set free from a mixture of solutions of potassium iodide and iodate by beryllium salts, as shown in the following equation:—

$3\text{BeSO}_4 + 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{Be}(\text{OH})_2 + 3\text{K}_2\text{SO}_4 + 3\text{I}_2$
The reaction proceeds slowly in the cold, but when the mixture is warmed and the iodine is removed with thiosulphate it is complete in a few minutes, even in dilute solutions. The precipitate of beryllium hydroxide settles quickly, and allows of rapid filtration and washing. The solution in which the beryllium is to be determined must be neutral or very faintly acid; if it contains excess of acids it must be neutralised with caustic soda till a precipitate begins to form, and this must then be dissolved in a few drops of dilute hydrochloric acid. Then an excess of a mixture of equal parts of 25 per cent potassium iodide and saturated potassium iodide solution is added (containing about 7 per cent of iodate). After five minutes the iodine separated is accurately decolorised with 20 per cent

sodium thiosulphate solution, and a little more of the iodide-iodate mixture is added in order to show that no more iodine can be separated. Then a small excess of thiosulphate is introduced, and the mixture heated on a water-bath. The precipitate is filtered off, washed with boiling water, dried, and ignited.

Analytical Examination of High Percentage Gases.—Alfred Stock and Carl Nielsen.—The ordinary absorption methods of determining gases are inaccurate because of the solvent power of water on gases, especially air. This inaccuracy becomes very great when pure or very high percentage gases are used. The authors suggest an improved apparatus for their estimation. Thus, to determine accurately a gaseous residue of less than 1 per cent in oxygen they fuse to an ordinary Hempel's burette a measuring pipette of 1 c.c. volume. This is connected with a cock with capillary bore through which the gas is introduced. Instead of bringing back into the Hempel's burette the gaseous residue freed from oxygen in the gas pipette, they read its volume off in the 1 c.c. pipette. For the absorption of the oxygen they use either copper wire gauze in ammonia solution containing carbonate, or alkaline ferrotartrate solution. It is generally assumed that by boiling and cooling rapidly water can be freed from air, but the authors have found that air is again quickly absorbed when the water comes into intimate contact with air; for example, on filling a long gas-burette the water contains no air only as long as it is kept from contact with air.

Mixtures of Liquid Oxygen and Nitrogen.—Alfred Stock and Carl Nielsen.—Erdmann and Bedford have called attention to a physical affinity between liquid oxygen and liquid nitrogen, stating that liquid oxygen cannot be freed from dissolved nitrogen even by continued boiling. The authors have investigated this phenomenon. They prepared pure oxygen and liquefied it and then introduced first liquid and then gaseous nitrogen. Then to remove the nitrogen by boiling, they either warmed a thin platinum-wire in the liquid by an electric current, or they led gaseous hydrogen in, or finally gaseous oxygen into the solution. The last method was naturally the most convenient. They found that when liquid oxygen mixes with nitrogen a rise of temperature occurs, but the nitrogen can be completely boiled out of the mixture, though if liquid air is used the argon makes the separation more difficult.

Autoxidation and Oxidation with Nitric Oxide.—W. Manchot.—In the autoxidation of organic compounds of the type RH_2 , one molecule of hydrogen peroxide results from the absorption of one molecule of oxygen, according to the equation $RH_2 + O_2 = R + H_2O_2$. According to this equation the linking of two oxygen atoms in the oxygen molecule leads to the formation of the hydrogen peroxide. This assumption can be experimentally investigated, if instead of gaseous oxygen an oxidising agent is used in which no such linking can take place. Nitric oxide can be employed for this purpose, and the author has examined its action on oxanthranol and indigo-white, and has proved that no hydrogen peroxide is formed. The reaction was found to occur quantitatively according to the equation $RH_2 + 2NO = R + H_2O + N_2O$. These experiments are of great importance for the theory of autoxidation. They prove definitely that the formation of hydrogen peroxide in these processes is due to the fact that the chain of two atoms of oxygen present in the oxygen molecule remains intact during the reaction, and is still retained in the hydrogen peroxide.

Sulphuric Acid Contact Process.—Lothar Wöhler, A. Foss, and W. Plüddemann.—The authors have compared the catalytic effect of platinum as metal, monoxide, and dioxide, and have found that the monoxide at first shows only one-fifth of the activity of the metal; while the action of the metal remains nearly constant during an experiment, that of the monoxide is greatly increased till it is equal to the action of the metal. The action of the

dioxide is even less than that of the monoxide, but it also increases. When palladium was substituted for platinum the results obtained were exactly analogous. If the catalytic action of the metal depended upon the intermediate formation of PtO or PtO_2 a better result would have been obtained by using the oxides than the metal, which is not the case. At first the action occurs according to the equation $PtO + SO_2 = SO_3 + Pt$, and then the metal is able to act catalytically. Thus the oxides of palladium and platinum are only pseudo-catalysers, *i.e.*, substances which by chemical reactions in the course of the process are converted into genuine catalysers. By investigating the action of the three metals, Pt, Pd, and Ir, at different temperatures between 450° and 750° on the contact mixture, the authors have deduced their curves of catalytic action. The temperature of maximum catalytic action is greatest with palladium and least with platinum, iridium being intermediate.

MISCELLANEOUS.

Cecil Medal and Prize.—We wish to draw our readers' attention to an announcement in our advertising columns respecting the award of the Cecil Medal and a prize of £5 which are to be awarded in 1907 for the best paper on "Chemistry as Applied to Sanitation and Domestic Purposes, *viz.*, Improved Cottages, Air, Water, and Drainage." There are few more useful applications of chemistry to the solution of social problems than those for which these prizes are to be awarded.

MEETINGS FOR THE WEEK.

MONDAY, 26th.—Society of Arts, 8. (Cantor Lectures). "Artificial Fertilisers—their Nature and Functions," by A. D. Hall.

WEDNESDAY, 28th.—Society of Arts, 8. "Patent Law Reform," by J. W. Gordon.

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THE COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF GOLD.

By RALPH NELSON MAXSON.

APPLICATION of the colorimetric method for the estimation of small amounts of gold, based upon the purple of Cassius coloration, have been proposed by Carnot (*Comptes Rendus*, xcvi., 105, 169), Rose (*CHEMICAL NEWS*, lxi., 271), Sonstadt (*CHEMICAL NEWS*, xxvi., 159), Cassel (*Eng. and Min. Journ.*, 76, xviii., 661), Prister (*Journ. Chem. Met. and Min. Soc. of South Africa*, 1903, iv., 235), Moir (*Journ. Chem. Met. and Min. Soc. of South Africa*, Sept., 1903), and others, but the use of this reaction for such a purpose is open to objection. According to the authority of other workers, the coloration thus produced is extremely variable, varying in intensity and shade according to the condition of the solution and precipitant. Moreover, the substance is unstable, and artificial standard solutions are necessary if accurate results are to be obtained.

It has been suggested that the coloration of red colloidal gold suspensions might have a quantitative relation to the amount of metal present, and a method of colorimetric estimation, free from the objections stated above, be based upon this relation. The following investigation was therefore undertaken in the hope of discovering whether such a relationship would not offer a suitable means for the estimation of small amounts of gold.

The preparation of the red colloidal suspensions was naturally the first object of interest. Blake (*Am. Journ. Sci.*, 1903, xvi., 381) has shown that acetylene is the most suitable reagent for effecting the reduction of the auric salt, the treatment consisting in drying the chloride at 170°, dissolving in ether, and pouring the ethereal solution into water also containing ether and saturated with acetylene gas. The use of ether was objectionable for the purpose of this investigation, and the simpler procedure described below gave good results.

The measured quantity of a standard solution of the auric salt was drawn off into a calibrated flask, and treated with a suitable amount of an aqueous solution of acetylene, made by dissolving the previously washed gas in water distilled and cooled in tin. The colour having developed, the solution was shaken, and the flask filled to the mark. The gold solutions used in these experiments were prepared from pure gold chloride, which contained hydrogen chloride in the usual amounts, and had not been subjected to a preliminary drying. The standard of these solutions was determined gravimetrically by means of magnesium ribbon, and by the electrolytic process with the revolving cathode. Solutions of less concentration were then obtained by suitable and accurate dilution.

A preliminary series of qualitative and quantitative experiments gave evidence that the coloration was of a quantitative nature, and that the suspensions were sufficiently stable under suitable conditions.

The Gallenkamp colorimeter was used in the subsequent quantitative experiments immediately following. The delicacy of the readings was increased by placing the instrument in a light-tight box pierced with suitably situated holes; the influence of external colours was avoided by admitting light to the instrument from a ground glass plate, which was found to be very efficient.

It is a well known fact that small amounts of electrolyte will rapidly change "red" gold to the "blue" modification. It is necessary therefore to conduct the comparisons in a room reasonably free from fumes, and to have all con-

taining vessels free from soluble material. It was found that flasks which had been treated with steam for a few minutes gave the best results. Red suspensions contained in such flasks gave no trace of blue after an interval of several weeks.

Using the precautions outlined above, the results shown in Table I. were obtained. The error of the personal equation was determined by means of a series of comparisons conducted with different concentrations of the same suspension, and covering a range of amounts of material identical with the amounts handled in the experiments given below.

TABLE I.

No.	Strength of solution. Per cent.	Gold taken.		Gold found.		Error.	Gold in i. c. c. of standard. Grm.
		Grm.	Grm.	Grm.	Grm.		
1.	99.6	0.00080	0.00086	+0.00006			0.000086
2.	95.5	0.00077	0.00082	+0.00005			
3.	90.9	0.00075	0.00078	+0.00003			
4.	85.7	0.00073	0.00074	+0.00001			
5.	84.3	0.00071	0.00073	+0.00002			
6.	67.6	0.00062	0.00058	-0.00004			0.000086
7.	63.4	0.00058	0.00055	-0.00003			
8.	56.0	0.00054	0.00048	-0.00006			
9.	52.0	0.00052	0.00045	-0.00007			
10.	47.9	0.00047	0.00041	-0.00006			
11.	98.6	0.00081	0.00085	+0.00004			
12.	88.2	0.00075	0.00076	+0.00001			
13.	78.8	0.00070	0.00068	-0.00002			
14.	71.6	0.00065	0.00062	-0.00003			
15.	66.1	0.00059	0.00057	-0.00002			
16.	60.4	0.00054	0.00052	-0.00002			
17.	57.8	0.00048	0.00050	+0.00002			
18.	49.8	0.00043	0.00043	0.00000			
19.	44.1	0.00038	0.00038	0.00000			
20.	36.4	0.00032	0.00031	-0.00001			
21.	98.6	0.00081	0.00085	+0.00004			0.000086
22.	88.2	0.00075	0.00076	+0.00001			
23.	78.8	0.00070	0.00068	-0.00002			
24.	71.6	0.00065	0.00062	-0.00003			
25.	66.1	0.00059	0.00057	-0.00002			
26.	60.4	0.00054	0.00052	-0.00002			
27.	57.8	0.00048	0.00050	+0.00002			
28.	49.8	0.00043	0.00043	0.00000			
29.	44.1	0.00038	0.00038	0.00000			
30.	36.4	0.00032	0.00031	-0.00001			
31.	87.8	0.00030	0.00030	0.00000			0.000034
32.	79.1	0.00028	0.00027	-0.00001			
33.	71.7	0.00026	0.00024	-0.00002			
34.	63.1	0.00024	0.00022	-0.00002			
35.	57.6	0.00022	0.00020	-0.00002			
36.	46.6	0.00019	0.00016	-0.00003			0.000034
37.	44.6	0.00017	0.00015	-0.00002			
38.	35.8	0.00015	0.00012	-0.00003			
39.	28.9	0.00013	0.00010	-0.00003			
40.	16.4	0.00004	0.00006	+0.00002			0.000034
41.	21.9	0.00007	0.00007	0.00000			
42.	25.9	0.00009	0.00009	0.00000			
43.	36.9	0.00011	0.00013	+0.00002			
44.	46.5	0.00013	0.00016	+0.00003			
45.	38.3	0.00015	0.00013	-0.00002			
46.	47.3	0.00017	0.00016	-0.00001			
47.			(Lost by accident).				
48.	56.8	0.00022	0.00019	-0.00003			
49.	66.1	0.00024	0.00023	-0.00001			

The forty-nine analyses given in the table were made under widely varying conditions. The age of the suspensions varied from a few minutes to several weeks. In order to avoid error of measurement, new standard suspensions were prepared from time to time, and their concentrations are shown in the last column of the table.

The analyses covered a wide range in amounts of gold, and were conducted under varying conditions of light. The results are seen to run with fair regularity, and the errors are approximately of the same order of magnitude.

The Gallenkamp colorimeter, used in the foregoing experiments, is not only expensive but cumbersome and complicated in construction; moreover, the instrument is not suitable for the correct estimation of the most minute amounts of gold, the colour becoming too faint for accurate comparison because of the shortness of the columns of liquid. A modified form of the type of apparatus proposed by Penfield for the colorimetric estimation of titanium, and consisting of comparison tubes set vertically in a dark box and illuminated from below, was therefore adopted. The tubes used in these comparisons had a diameter of 1 c.m. and a length of 13 c.m., and were accurately graduated to hold 10 c.c.

A mirror suitably situated beneath the box containing the tubes gave efficient illumination. Such an apparatus is not only cheaply and easily procured, but if tubes of these dimensions are used it is capable of accurately determining very small amounts of gold.

The method of comparison was carried out in the following manner:—A measured amount of the suspension was drawn off into the left-hand tube and diluted to the mark with water; a suitable amount of water was then placed in the right-hand tube, and the standard suspension drawn into the tube until the colours were seen to be identical. The necessary amount of water to be used can be determined by preliminary experiment.

The positions of the tubes were always reversed before the final reading was taken.

The following experiments were made in order to determine the error and range of amounts of gold capable of accurate estimation in such an apparatus with tubes of the dimensions described above. The comparisons were made with a red suspension prepared by careful dilution of a more concentrated standard suspension which contained 0.0000175 grm. of metal in 1 c.c.

The results obtained with different concentrations of the standard suspension just described are given in Table II.

TABLE II.

No.	Gold sus- pension analysis. taken.	Gold sus- pension used.	Gold found.			Error.
			C.c.	Grm.	Grm.	
1.	9.50	9.05	0.000102	0.000097	-0.000005	
2.	8.00	7.59	0.000086	0.000082	-0.000004	
3.	7.00	6.89	0.000075	0.000074	-0.000001	
4.	6.00	5.83	0.000065	0.000063	-0.000002	
5.	5.00	4.84	0.000054	0.000052	-0.000002	
6.	4.00	3.88	0.000043	0.000042	-0.000001	
7.	3.00	2.47	0.000032	0.000027	-0.000005	
8.	2.00	1.82	0.000022	0.000020	-0.000002	
9.	1.00	0.93	0.000011	0.000010	-0.000001	

The intensity of the colour in the above experiments ranged from a deep red to a faint pink. Further comparisons made with suspensions more dilute than those described above gave errors of magnitude increasing with the dilution. The amounts handled here are, then, the minimum quantities that can be accurately estimated with the apparatus described. It is obvious that if larger amounts of the metal are to be determined, tubes of greater dimensions should be used.

The application of such a method for the determination of gold naturally starts with that element. The weighed amount of metal, contained in a clean porcelain crucible, can be readily brought into solution with the aid of chlorine water or aqua regia, and the excess of the solvent evaporated off upon the water-bath. Experiments have shown that a gentle preliminary heating of the solution of the auric salt hastens the rapidity of the reduction. Care must be taken not to reduce any of the gold chloride by such a procedure.

If traces of electrolyte are present the coagulation of the "red" gold may be sometimes avoided by the addition of a few drops of ether to the cold solution. When small amounts of the metal are handled the volume of the solution should not exceed a few c.c., and only a small amount

of the aqueous solution of acetylene should be added; otherwise the coloration may be partially or totally inhibited.

In conclusion, it can be seen from the evidence of the experiments described above, that the colorimetric estimation of small amounts of gold is quantitatively possible if proper precautions are taken to ensure the maximum coloration and exclusion of electrolytes. The method is quick and simple in character, and for the amounts of gold used above, the results show it to possess suitable accuracy for the correct estimation of small amounts of the metal.

The author wishes to acknowledge his indebtedness for much helpful aid and advice in this, and in previous work, to Prof. Gooch, at whose suggestion these experiments have been carried on.—*American Journal of Science*, xxi., p. 270.

THE VOLHARD METHOD FOR THE DETERMINATION OF CHLORINE IN POTABLE WATERS.

By FRANK T. SHUTT, M.A., F.I.C.,
and
H. W. CHARLTON, B.A.Sc.

In judging of the purity of a water supply the chlorine content, as is generally admitted, is a factor of the greatest importance. It is of especial value when comparing waters from adjacent sources or those collected at different points from the same source—as from a river or lake. In such cases a difference of a few parts per million of chlorine may be sufficient to establish sewage contamination. It becomes, therefore, a matter of the greatest consequence that the water analyst should be possessed of a process whereby he can determine the chlorine with accuracy.

The process practically in universal use for the estimation of chlorine in waters is that known as the "chromate" method—a description of which is to be found in all works on water analysis. In the majority of cases this method is eminently satisfactory, but there are some waters with which it fails to give a sufficiently close reading for diagnostic purposes, and again others with which it is altogether impossible to obtain a definite end reaction. We have, for instance, found that the chromate method is extremely unsatisfactory, practically valueless, for many "upland surface" waters, namely, those brown from dissolved peaty matter and characterised by a low chlorine content.

To learn if more satisfactory results could not be obtained, particularly with peaty waters, we recently adapted the Volhard method, and have since examined by it more than sixty samples representative of all classes of potable waters. In this we have met with gratifying success, for in no case has it been found to fail. Duplicate determinations agree very well, the end reaction being sharp and easily noted. Indeed, it is safe to say that if the Volhard were as rapid as the chromate method it would soon replace it. Our opinion is, however, that its usefulness is rather as an auxiliary or supplementary method than one to replace entirely the older process.

The Volhard Method.

Solutions.—The same silver nitrate solution is used as is employed in the chromate method, viz., of such a strength that 1 c.c. = 0.001 chlorine.

A solution of potassium sulphocyanide, of such a strength that 1 c.c. corresponds to 1 c.c. of the silver nitrate solution. (NOTE.—Ammonium sulphocyanide cannot be used).

Nitric acid (three volumes of acid to one of water). This is boiled to expel oxides of nitrogen. This, as also the above solutions, should be kept in the dark.

The indicator is made by dissolving ferrous sulphate in water and completely oxidising by nitric acid on the water-bath. It is then evaporated to dryness repeatedly with a

little concentrated sulphuric acid to expel the excess of nitric acid, and ferric carbonate added to neutralise the sulphuric acid. The solution is then filtered and is ready for use.

Modus operandi.—100 c.c. of the water to be examined are poured into a beaker and 5 c.c. to 10 c.c. of the nitric acid added. Then, from a 2 c.c. pipette graduated to 1/50 c.c., a slight excess of silver nitrate solution is added. After a few minutes, the precipitated chloride is filtered out and well washed, the filtrate being received in a porcelain basin. (The filter-pump may frequently be used to advantage). To this is now added one c.c. of the indicator and the potassium sulphocyanide solution run in (from a similar pipette to that used with the silver nitrate) until a faint red colour is permanently produced. The end-point is sharp and easily noted. The difference between the number of cubic centimetres of the silver nitrate and of the potassium sulphocyanide solutions used represents the number of cubic centimetres of the former required by the chlorine in 100 c.c. of the water.

To ascertain the relative accuracy of the chromate and Volhard methods, a series of determinations were made on certain dilute solutions of chemically pure sodium chloride, with the results given in Table I.

TABLE I.—Chlorine (Parts per Million).

Chlorine added as sodium chloride.	Found by Volhard method.	Found by chromate method.
36.4	36.8	37.5
24.3	24.8	26.0
13.1	13.0	14.0
12.1	12.2	14.0
6.1	6.7	7.0
6.0	6.5	7.0
3.6	3.8	4.6
3.6	3.5	4.8
2.4	2.5	3.3
1.2	1.25	0.5
1.2	1.0	0.6
0.6	0.5	} Could not be determined with precision.
0.6	0.5	
0.5	0.6	
0.25	0.125	
0.25	0.175	

These data are sufficient, we think, to show the extreme sensitiveness of the Volhard method and also its superiority to the chromate process, especially when very small amounts of chlorine are to be determined.

Some of our earlier trials with this method were made on upland peaty waters—a class with which, as we observed, it is very difficult to obtain satisfactory results by the older process. The accompanying series (Table II.), consisting of samples taken from various points on the same river, very well illustrates the value of the Volhard method. All the waters were quite brown from the presence of dissolved peaty matter, but with the Volhard process this high colour did not interfere with the end reaction, as happened when using the chromate method.

TABLE II.—Analysis of Peaty Waters (Results in Parts per Million).

	Free ammonia.	Albumenoid ammonia.	Nitrogen as nitrites and nitrates.	Chlorine by—		Solids.	
				Volhard.	Chromate.	At 212° F.	After ignition.
A.	0.06	0.133	0.092	2.3	1.9	70.0	36.4
B.	0.088	0.166	0.0297	2.3	1.6	75.6	35.8
C.	0.03	0.14	0.0294	2.2	1.3	69.2	33.2
D.	Free	0.138	0.05	1.6	0.95	64.4	32.4
E.	0.01	0.24	0.024	2.0	0.64	75.2	32.0
F.	0.044	0.256	0.0131	2.5	0.61	64.8	34.8
G.	0.05	0.208	0.0082	2.2	0.60	75.2	31.2

Comparing the chlorine values, it will at once be seen that the Volhard results allow a much closer discrimination

than is possible from those of the chromate method. In this instance they were instrumental in establishing the entrance of sewage at a certain point in the course of the river—a fact which the chromate data were quite incapable of showing.

The results given in Table III. have been taken seriatim from our analysis book, and constitute about two-thirds of the waters examined by the Volhard process to date. The waters are from all sources and come from all parts of the Dominion. Among them are representatives of the polluted barnyard well, of pure spring waters, of river and lake waters, and of waters charged with saline matter and occasionally sulphuretted hydrogen.

TABLE III.—Chlorine in Potable Waters (Parts per Million).

No.	By chromate method.	By Volhard method.
1.	32.0	31.2
2.	38.0	40.0
3.	22.0	22.5
4.	*	3.5
5.	90.0	90.0
6.	45.0	45.0
7.	80.0	80.0
8.	5.0	4.5
9.	39.0	45.0
10.	19.0	18.0
11.	142.5	140.0
12.	18.0	18.0
13.	9.5	8.0
14.	26.0	25.0
15.	85.0	82.0
16.	*	4.5
17.	17.0	16.2
18.	17.0	16.0
19.	*	0.6
20.	100.0	102.0
21.	9.0	8.7
22.	5.0	4.5
23.	95.0	95.0
24.	30.0	28.2
25.	58.0	60.0
26.	32.0	29.2
27.	1.0	1.5
28.	*	16.0
29.	3.2	3.0
30.	255.0	252.0
31.	3.0	2.0
32.	1800.0	1750.0
33.	200.0	175.0
34.	510.0	505.0
35.	*	1.0
36.	165.0	162.0
37.	13.0	13.0
38.	3.5	2.8
39.	*	32.0
40.	34.0	29.0

In the waters marked * the chlorine could not be determined with any degree of accuracy by the chromate method.

In a large number of these examples the results by the chromate method are sufficiently accurate for ordinary purposes, but the very fact that among these waters there were five the chlorine of which could only be satisfactorily determined by the Volhard process emphasizes the value of this latter method for water analysis.

It is to be observed that the particular usefulness and accuracy of this process is with waters containing very small amounts of chlorine—a fact which enhances its importance for the examination of upland surface waters, which are naturally low in chlorides.

In the Volhard method no check or blank is required, and hence one source of error is avoided. In the chromate method the check may require from 0.2 to 0.5 c.c. silver

nitrate solution, according to the character of the distilled water. This means, if only 10 c.c. of the water were under examination, a possible error of 30 parts per million.

With the chromate method 100 c.c. of the water sample is commonly employed for the titration, smaller quantities being taken of waters with high chlorides and made up to that volume. The Volhard does not necessitate any fixed volume for titration, and experience has shown that the filtrate and washings may vary from 80 c.c. to 120 c.c. without affecting in the least the results.

Our custom now in the laboratories of the Experimental Farms is to examine all the waters received for analysis by the chromate method; if a satisfactory end reaction is obtained the results are accepted as correct. If, however, difficulty is met with in this particular the Volhard process is employed, and in no instance has the latter failed to give a reading at once clear and decisive.—*Transactions of the Royal Society of Canada*, xi., p. 67.

A REVISION OF THE ATOMIC WEIGHT OF BROMINE.*

By GREGORY PAUL BAXTER.

In numerous investigations in this laboratory upon the atomic weights of certain metals, in which metallic bromides were first titrated against the purest silver, and then the precipitated silver bromide was collected and weighed, the relation between the silver used in the titrations and the silver bromide obtained has yielded data from which the atomic weight of bromine may be calculated. Furthermore, in all these investigations, as a check upon the purity of the silver and bromine employed, silver bromide was synthesised directly from weighed quantities of silver and an excess of ammonium bromide or hydrobromic acid. Many of these results have already been collected and discussed by Richards (*Proc. Am. Phil. Soc.*, 1904, xliii., 119); nevertheless, they are cited in the accompanying table together with a few more recent determinations.

From the first of these ratios the atomic weight of bromine, referred to silver 107.930, is found to be 79.956, and from the second 79.955.

Very recently, in experiments in which silver iodide was heated first in a current of air and bromine until the iodine was completely displaced, and then in a current of chlorine to displace the bromine, the ratio of silver bromide to silver chloride was determined in six cases. From the results of these experiments the atomic weight of bromine was calculated to be 79.953 (Baxter, *Journ. Am. Chem. Soc.*, 1905, xxvii., 884), if the atomic weight of chlorine is assumed to be 35.473 (Richards and Wells, Publications of the Carnegie Institution, 1905, No. 28; *Journ. Am. Chem. Soc.*, xxvii., 459).

These values for bromine are in close agreement with those of Stas ("Œuvres Complètes," i., 603). In his experiments weighed quantities of pure silver and bromine were first titrated against each other, and then the precipitate of silver bromide was collected and weighed. Of the four results by the first method, one should be rejected according to his own statements, since the bromine was not thoroughly dried. The remaining three, 79.959, 79.961, and 79.960, gave as an average 79.960. From the weight of silver bromide four values were obtained, 79.950, 79.952, 79.955, and 79.957, with an average of 79.954.

Marignac ("Œuvres Complètes," i., 181) also determined the ratio of silver to silver bromide, with somewhat lower results—79.959, 79.941, and 79.952; average, 79.950.

Scott (*Journ. Chem. Soc.*, 1901, lxxix., 147), in his analysis of ammonium bromide, obtained six values for the

Bromide analysed.		Number of experiments.	Ratio, Ag:AgBr.
<i>Indirect Determinations.</i>			
1.	BaBr ₂	Last seven ..	57.444
2.	SrBr ₂	Seven	57.444
3.	ZnBr ₂	One	57.445
4.	NiBr ₂	Seven	57.444
5.	CoBr ₂	Last five	57.446
6.	UBr ₄	Three	57.447
7.	CsBr	Three	57.444
8.	FeBr ₂	Two	57.443
9.	CdBr ₂	Eight	57.444
10.	MnBr ₂	Thirteen	57.444

Average, weighted according to the number of determinations 57.4443

Direct Determinations.

11.	HBr	Two	57.445
12.	NH ₄ Br	One	57.446
13.	HBr	Two	57.444
14.	NH ₄ Br	One	57.445
15.	NH ₄ Br	One	57.444
16.	NH ₄ Br	Two	57.447
17.	NH ₄ Br	Three	57.444
18.	NH ₄ Br	One	57.443

Average, weighted according to the number of determinations 57.4447

Analyst and Reference.

1. Richards, *Proc. Am. Acad.*, xxviii., 28.
2. Richards, *Ibid.*, xxx., 389.
3. Richards, *Ibid.*, xxxi., 178.
4. Cushman, *Ibid.*, xxxiii., 111.
5. Baxter, *Ibid.*, xxxiii., 127.
6. Merigold, *Ibid.*, xxxvii., 393.
7. Archibald, *Ibid.*, xxxviii., 466.
8. Baxter, *Ibid.*, xxxix., 252.
9. Hines, *Journ. Am. Chem. Soc.*, xxviii., 783.
10. Hines (not yet published).
11. Richards, *Proc. Am. Acad.*, xxviii., 17, 18.
12. Richards, *Ibid.*, xxx., 380.
13. Richards, *Ibid.*, xxxi., 165.
14. Cushman, *Ibid.*, xxxiii., 106.
15. Baxter, *Ibid.*, xxxiii., 122.
16. Baxter, *Ibid.*, xxxiv., 353.
17. Baxter, *Ibid.*, xxxix., 250.
18. Hines (not yet published).

same ratio, varying between 79.936 and 79.948, with an average of 79.943. One of his results is here rejected, since the silver used in this experiment was known to be impure.

Dumas (*Ann. Chem. Pharm.*, 1860, cxlii., 20), by heating silver bromide in chlorine, found the values 80.06, 79.89, and 79.96.

In computing the atomic weight of bromine from these data, great weight is always given to Stas's determinations, the value 79.955 being usually assumed as the most probable one for the constant in question. Certainly, as pointed out by Richards (*Proc. Am. Phil. Soc.*, 1904, xliii., 119), the true value must lie between 79.95 and 79.96. Clarke calculates the value 79.949 as the weighted average of the difference investigated previous to Scott's ("A Re-calculation of Atomic Weights," Smith. Misc. Coll., 1897).

Considerable uncertainty exists as to the purity of the materials employed in much of the foregoing work. Richards and Wells have already exhaustively investigated the various methods of preparing pure silver, and have found that while it is a comparatively simple matter to free this substance from metallic impurities, the absence of gaseous impurities is by no means so easy to secure

*From the *Journal of the American Chemical Society*, xxviii., No. 10.

(Publications of the Carnegie Institution, No. 28, 16; also *Journ. Am. Chem. Soc.*, 1905, xxvii., 472). Oxygen may be eliminated best by fusion in an atmosphere of pure hydrogen gas (Baxter, *Proc. Am. Acad. Arts Sci.*, 1903, xxxix., 249), or by prolonged fusion in a vacuum, while a lime-boat was found to be the most suitable support for the silver during fusion.

In most of the experiments cited on page 202, one of the final steps in the purification of the silver was fusion of electrolytic crystals on lime, in many cases in a vacuum, but without especial care to prolong the fusion. Silver prepared in this way was found by Richards and Wells to contain traces of oxygen, derived from silver nitrate occluded by the electrolytic crystals. In cases 8, 9, 10, 17, and 18, however, the silver was fused in hydrogen. Richards and Wells showed also that Stas's silver contained at least 0.01 per cent of impurity, since it yielded 0.01 per cent less silver chloride than their purest silver (*loc. cit.*, p. 62). Scott's silver in three cases was merely heated, not fused, in hydrogen, and in two of the others was fused before a blowpipe on calcium phosphate. In one experiment only the metal was fused on lime. No details are given as to the purification of the silver used by Marignac.

Bromine also may be freed from impurities only with some difficulty. Experience in this laboratory has shown that chlorine may be eliminated most conveniently by distilling or precipitating the bromine from solution in a bromide. One such distillation is sufficient to remove chlorine completely only when the substance is initially comparatively pure. If, however, the process is repeated by converting a portion of the partially purified product into a bromide, and dissolving the remainder of the bromine in this comparatively pure bromide, the chlorine is eliminated so completely that further repetitions of this process have no apparent effect. (Attention has already been called to these points by Richards and Wells, *Proc. Am. Acad. Arts Sci.*, 1906, xli., 440). The removal of iodine may be easily effected by converting the bromine into hydrobromic acid or a soluble bromide, and boiling the solution with a small quantity of free bromine. Here again it is well to repeat the process several times, since the reaction between free bromine and the iodine ion, like that between free chlorine and the bromine ion, is undoubtedly incomplete.

The greater part of the experiments cited above were made with bromine which had been purified with due observance of these precautions. Of the other investigators, Stas seems to have been the only one to use sufficient pains to secure purity of the bromine. Stas removed iodine by shaking potassium bromide several times with free bromine and carbon disulphide, and in the course of the prolonged purification distilled the bromine twice from solution in a bromide. Marignac's purification consisted solely in crystallisation of barium bromate and Scott's in distillation of hydrobromic acid.

Of the methods employed in these early determinations, that involving the analysis of metallic halides is least suited for the purpose, on account of the danger of occlusion of metallic salts by the precipitated silver bromide. That such an error actually exists to a slight extent is shown by the fact that the average of the "indirect" determinations is slightly larger than the average of the "direct" determinations. Obviously, if silver bromide is precipitated by means of either ammonium bromide or hydrobromic acid, occluded ammonium salts or free acids could be easily expelled by fusion of the bromide. This precaution was observed in most of the determinations recorded on page 202, and is absolutely essential for the complete elimination of water from the salt. Stas and Marignac both fused the silver bromide in their syntheses, but this precaution was omitted by Scott, who dried the bromide at 180°. Scott's statement that the loss on fusion of silver bromide which had been dried at 180° was due to the presence of asbestos is contradicted by the experiments recorded later in this paper, in which the loss on fusion amounted to about 0.01 per cent in the case of silver

bromide which had been dried in a similar fashion, and which was almost entirely free from asbestos.

From this brief discussion of the more important errors which may have influenced previous determinations of the atomic weight of bromine, it is evident that some uncertainty still exists as to the true value of this constant. In the hope of throwing new light upon the subject, experiments were carried out by two of the methods outlined above, with especial precautions to insure purity of materials and to eliminate known possible errors in the experimental methods.

Both the methods chosen—synthesis of silver bromide from a weighed amount of silver, and conversion of silver bromide into silver chloride—have already been recently tested in this laboratory, and have been found to be at least as satisfactory as any (Baxter, *Proc. Am. Acad. Arts Sci.*, xl., 419; xli., 73; Richards and Wells, Publications of the Carnegie Institution, No. 28; *Journ. Am. Chem. Soc.*, 1905, xxvii., 876).

Purification of Materials.

Bromine.—In purifying bromine for this research, the principles set forth above of this paper were applied, but in some cases the purifying processes were repeated after the product was apparently pure, in order to make certain that further treatment had no effect.

Sample I. was first completely dissolved in calcium bromide which had been made from about one-third of the original material by means of lime and ammonia, and was then distilled from the solution. The product was covered with several times its volume of water, and was converted into hydrobromic acid by means of pure hydrogen sulphide which had been generated from ferrous sulphide with dilute sulphuric acid, and which had been thoroughly washed with water. After filtration from the precipitated sulphur and bromide of sulphur, the acid was boiled for some time, with occasional addition of small quantities of re-crystallised potassium permanganate to eliminate the iodine. Finally, the residual hydrobromic acid was heated with an equivalent amount of re-crystallised permanganate, and the bromine was condensed in a flask cooled with ice.

Sample II. was first converted into hydrobromic acid by means of red phosphorus and water, and the hydrobromic acid was then distilled, after having been boiled with an excess of bromine. An equivalent amount of permanganate was added, and the bromine liberated was separated from the solution by distillation. About one-fourth of the product was next transformed into calcium bromide by means of ammonia and lime which was free from chloride, and the remaining three-fourths of the bromine were dissolved in the calcium bromide and distilled. Still a third distillation from a bromide was carried out by reducing the product of the second distillation with hydrogen sulphide, and subsequently oxidising the hydrobromic acid with the purest re-crystallised potassium permanganate, after boiling the acid with several small portions of permanganate to eliminate the last traces of iodine.

Sample III. was obtained by preparing calcium bromide from a portion of Sample II. and distilling the remainder of Sample II. from solution in this bromide.

In the case of Sample IV. the processes of reduction to hydrobromic acid with hydrogen sulphide and oxidation of the hydrobromic acid with pure permanganate were four times repeated. After each reduction the hydrobromic acid was boiled with free bromine to remove iodine.

Sample V. was three times reduced with hydrogen sulphide and oxidised with permanganate. One-fourth the product was converted into calcium bromide and the remainder was dissolved in this calcium bromide and distilled.

Thus, Sample I. was twice distilled from a bromide; Sample II. was treated three times in the same way; and Sample III., IV., and V. four times.

Shortly before use each sample was distilled and converted into ammonium bromide by slow addition to an

excess of re-distilled ammonium hydroxide. The solution was then boiled to expel the excess of ammonia.

Silver.—Several different samples of silver were employed, many of which have already been used in atomic weight researches in this laboratory, and have shown evidence of great purity. For details concerning the purification the papers referred to should be consulted.

Sample A was employed in a determination of the atomic weight of iodine (Baxter, *Proc. Am. Acad. Arts Sci.*, 1904, xl., 420; *Journ. Am. Chem. Soc.*, 1905, xxvii., 881). This specimen had been twice precipitated as chloride, and once electrolysed.

Sample B was used in experiments upon the atomic weight of iodine (Baxter, *Proc. Am. Acad. Arts Sci.*, 1905, xli., 79; *Journ. Am. Chem. Soc.*, 1905, xxvii., 881) and of manganese (Baxter and Hines, this paper will soon be published). It was precipitated once as chloride, electrolysed once, and finally precipitated as metal with ammonium formate.

Sample C also was employed in a determination of the atomic weight of manganese, and was purified by recrystallising silver nitrate, seven times from nitric acid, and five times from aqueous solution. Finally, the silver nitrate was reduced by means of ammonium formate.

Sample D was prepared for the determination of the atomic weights of cadmium (Baxter and Hines, *Journ. Am. Chem. Soc.*, 1906, xxviii., 772; *CHEMICAL NEWS*, xciv., p. 224 *et seq.*) and manganese, by one precipitation as chloride, one precipitation with ammonium formate, and one electrolysis.

Sample E was first purified in part by precipitation as chloride, in part by precipitation with ammonium formate. The combined material was then subjected to two electrolyses.

In all cases the electrolytic crystals were fused in a boat of the purest lime, contained in a porcelain tube, in a current of electrolytic hydrogen. After the buttons had been cleansed with dilute nitric acid and dried at 200°, they were cut into fragments of from 4 to 8 grms. either by means of a clean chisel and anvil or with a fine jeweller's saw. The latter method was employed in the case of Samples D and E, because it proved easier completely to free the silver from surface contamination with iron by etching the fragments with nitric acid, than when a chisel was used. The cleansing process with nitric acid was repeated until the solution thus obtained, after precipitation with hydrochloric acid and evaporation, proved free from iron. That every trace of iron could be removed by this treatment was proved by testing for iron the evaporated filtrates from several of the analyses subsequently recorded in this paper. Negative results were obtained in all cases.

After thorough washing with water and drying at 100°, the pieces of metal were heated to about 400° in a vacuum, and were preserved over solid potassium hydroxide in a desiccator.

The Ratio of Silver to Silver Bromide.

The ratio of silver to silver bromide was determined as follows:—Weighed quantities of silver were dissolved in the purest re-distilled nitric acid, diluted with an equal volume of water, in a flask provided with a column of bulbs to catch possible spatterings. However, during the solution of the silver the temperature was kept so low that almost no gas was evolved, and hence there was very little danger from this source. Next the acid solution of the silver was diluted with an equal volume of water, and was heated until free from nitrous acid and oxides of nitrogen. After still further dilution, the solution was added slowly with constant agitation to a dilute solution of an excess of ammonium bromide in a glass-stoppered precipitating flask, and the whole was violently shaken for some time to promote coagulation. By adding the silver solution to the bromide, occlusion of silver nitrate was almost wholly precluded. In some experiments the solutions were as dilute

as twentieth-normal, in others as concentrated as fourth-normal. The final results seemed to be independent of the concentration of the solutions. At the end of about twenty-four hours the flask with its contents was again shaken, and then it was allowed to stand until the supernatant liquid was perfectly clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible, after thorough washing by decantation with water, and was dried in an electric oven, first for several hours at 130°, finally for about fourteen hours at 180°. Then it was cooled and weighed.

The operations of precipitation and filtration were performed in a large cupboard lighted with red light, and if the flask was taken out of this cupboard it was enveloped in several thicknesses of black cloth.

Even after the prolonged drying, traces of moisture were retained by the salt, and could be expelled only by fusion. This was done by transferring the bulk of the silver bromide, freed as completely as possible from asbestos, to a small porcelain crucible which was weighed with its cover. The silver bromide was then fused by heating the small crucible, contained in a large crucible to prevent direct contact with the flame of the burner. A temperature much above the fusing-point of silver bromide was avoided so that the volatilisation of the salt could not take place. This treatment must have eliminated occluded ammonium salts as well as water. Finally, in order to convert any occluded silver nitrate, metallic silver, or silver sub-bromide into silver bromide, the salt was again fused in a current of dry air containing bromine vapour. This treatment seldom produced any measurable effect either upon the weight or the appearance of the salt, which was perfectly transparent and of a light yellow colour even after the first fusion in air.

A few shreds of asbestos displaced from the crucible, together with an occasional trace of silver bromide which escaped the crucible, were collected upon a tiny filter-paper, which was then ignited in a porcelain crucible. Before being weighed the ash was either treated with a drop of nitric and hydrobromic acids, and again heated, or else was heated for some minutes in a current of air and bromine.

The filtrate and washings were evaporated to small bulk. The precipitating flask and all other glass vessels used in the analysis were rinsed with ammonia, and the rinsings were added to the evaporated filtrate and wash-waters. The whole was then tested in a nephelometer for silver and the quantity found was estimated by comparison with standard silver solutions. In most cases the correction thus obtained was less than 0.1 m.grm.

The asbestos which formed the felt in the Gooch crucible, after having been shredded, was digested for some hours with aqua regia and was then thoroughly washed with water. Before the empty crucible was weighed the felt was ignited with a Bunsen burner. Crucibles thus treated and then heated to 180° after being moistened with water did not change in weight.

In Table I. are cited all the analyses which were completed without accident. Vacuum corrections of -0.000031 for every apparent grm. of silver and of +0.000041 for every apparent grm. of silver bromide are applied. The atomic weight of silver is assumed to be 107.930.

(The specific gravity of the weights was determined to be 8.3. The specific gravity of silver has been found to be 10.49—Richards and Wells. Publications of the Carnegie Institution, No. 28, 11. The specific gravity of fused silver bromide has been found to be 6.473—Baxter and Hines, *Am. Chem. Journ.*, xxxi., 224).

The platinum plated brass weights were standardised from time to time, and were found to retain their original values within a very few hundredths of a milligram. in all cases.

(To be continued).

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting November 15th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MESSRS. J. Campbell Brown and W. H. Hurtle were formally admitted Fellows of the Society.

Certificates were read for the first time: in favour of Messrs. Frank Stanley Benton, Hurstead, Reigate; John Trevor Cart, B.Sc., A.I.C., 4, Simonside Terrace, Heaton, Newcastle-on-Tyne; George William Clough, B.Sc., 29, Oseney Crescent, N.W.; Victor George Jackson, 21, Frankfurt Road, Herne Hill, S.E.; Louis Murgatroyd, 1, Carlton Drive, Heaton, Bradford; Robert Robertson, M.A. D.Sc., F.I.C., 9, Sewardstone Road, Waltham Abbey; Arthur Henry Salway, Ph.D., B.Sc., 15, Palmerston Road, Forest Gate, E.; Robert Low Smith, 56, Genesta Road, Plumstead, S.E.; William Sandilands Templeton, M.A., B.Sc., Colombo, Ceylon; Maximilian Toch, 261, West 71st Street, New York City, U.S.A.

A certificate was authorised by the Council for presentation to ballot under By-law I. (3) in favour of Tarak Nath Majumdar, 37, Lower Chitpore Road, Calcutta, India.

Of the following papers, those marked * were read:—

*203. "The Determination of the Rate of Chemical Change by Measurement of Gases Evolved." (Preliminary Notice). By FRANCIS EDWARD EVERARD LAMPLOUGH.

The most important results of this investigation may be summarised as follows:—

When a chemical reaction takes place in solution resulting in the formation of a substance which is gaseous at the ordinary temperature, the solvent becomes supersaturated with the gas.

The degrees of supersaturation may be so great that the solvent contains one hundred times the normal amount of the gas, and from such a solution the gas is gradually evolved.

The excess of gas so dissolved may be almost entirely expelled in thirty seconds by briskly agitating the liquid.

Investigation of the rate of decomposition of hydrogen peroxide showed that under such conditions of efficient stirring, the rate of evolution of a gas furnishes an accurate and reliable method of investigating reactions of this nature.

The decomposition of diazobenzene chloride was shown to be strictly a unimolecular reaction throughout, the rate of which is independent of the amount of acid present. The value of the constant for the reaction was found to vary with change of temperature, increasing logarithmically with increase of temperature.

The nature of the decomposition of ammonium nitrite most nearly approaches that of a quadrimolecular reaction throughout the extent of decomposition investigated.

The decomposition of formic acid by sulphuric acid is a true unimolecular reaction, and not bimolecular, as it has been hitherto considered.

The reaction between nickel carbonyl and iodine has also been studied.

DISCUSSION.

Dr. CAIN pointed out that Hantzsch had first shown that the value of the constant obtained in measurements of the rate of decomposition of diazo solutions was low at the beginning of an experiment, owing to the solubility of the nitrogen. There was no supersaturation, however, in the solutions used in the experiments by him (Dr. Cain) and Mr. Nicoll, for the deficit in the quantity of nitrogen evolved corresponded to the amount which would ordinarily remain in solution. Moreover, the values obtained for the constants agreed well with those given by Hantzsch, Euler, and other investigators.

Mr. CALDWELL asked if there were any *real* retardation of these reactions when the solutions were not stirred. The accumulation of large amounts of the gaseous product existing in a highly supersaturated state in the solution might tend to make a reaction reversible.

Mr. LAMPLOUGH, in reply, stated that the method adopted for the preparation of the diazobenzene chloride was that described by Dr. Cain in his paper. The solution was raised to the desired temperature in fifteen to thirty seconds.

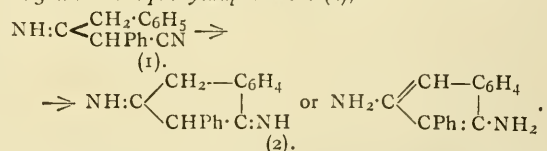
As evidence that supersaturation was really present the author referred to an actual comparison experiment, showing the volume of gas evolved from solutions stirred and not stirred, where it was seen from the lantern-slide exhibited that at one time 37 c.c. of the solution at 62° held supersaturated 22 c.c. of nitrogen, or more than thirty times the amount calculated from the solubility of the gas. The author also gave numbers showing the great difference between his constants for the reaction and those determined by Cain and Nicoll.

A reaction resulting in the evolution of carbon dioxide had been studied, but owing to the greater solubility, the degree of supersaturation was small, and at present the author had not sufficient data to say whether a highly supersaturated solution is more easily formed in the case of the more insoluble gases.

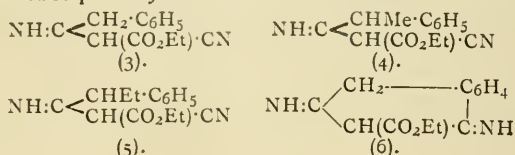
In the comparison experiments on the decomposition of hydrogen peroxide in which the rates of reaction were determined by measurement of the gas evolved from the stirred solution and by titration respectively, in the latter case the solution was *not* stirred, and therefore the close agreement in the results showed that the rate of evolution of gas from the stirred solution also measured truly the rate of reaction in the still liquid. Moreover, if the reaction is allowed to begin without agitation and at a given time the solution is suddenly stirred, an immediate evolution of gas takes place, making the total volume of gas evolved equal to the amount given off in the same time *with* stirring, thus showing that stirring does not influence the rate of the reaction, but simply gives a correct method of measuring it.

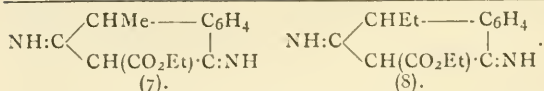
*204. "The Formation and Reactions of Imino-compounds. Part II. Condensation of Benzyl Cyanide leading to the Formation of 1:3-Diaminonaphthalene and its Derivatives." By ERNEST FRANCIS JOSEPH ATKINSON and JOCELYN FIELD THORPE.

Benzyl cyanide condenses with its sodium derivative to form β -imino- α -cyano- γ -diphenylpropane (1), which on treatment with sulphuric acid is completely converted into 1:3-diamino-2-phenylnaphthalene (2),—

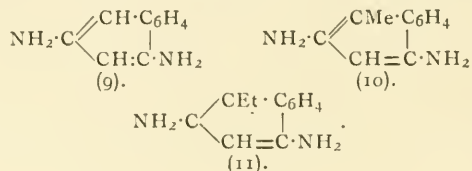


Benzyl cyanide also combines with the sodium derivative of ethyl cyanoacetate, forming ethyl β -imino- α -cyano- γ -phenylbutyrate (3), from which on treatment with sodium ethoxide and either methyl or ethyl iodide, ethyl β -imino- α -cyano- γ -phenylmethylbutyrate (4), or ethyl β -imino- α -cyano- γ -phenylethylbutyrate (5) can be prepared. From these compounds on treatment with sulphuric acid ethyl 1:3-diaminonaphthalene-2-carboxylate (6), ethyl 1:3-diamino-4-methylnaphthalene-2-carboxylate (7), and ethyl 1:3-diamino-4-ethylnaphthalene-2-carboxylate (8) are formed respectively:—





The ethyl esters (6), (7), and (8) are converted on hydrolysis into the corresponding *carboxylic acids*, which on heating above their melting-points are transformed into 1:3-diaminonaphthalene (9), 1:3-diamino-4-methylnaphthalene (10), and 1:3-diamino-4-ethylnaphthalene (11), respectively:



DISCUSSION.

The PRESIDENT pointed out that the very elegant synthetical method of obtaining 1:3-diaminonaphthalene made known by the authors might prove of great practical use in preparing this base in quantity. The method hitherto available, in which dinitro- α -acetonaphthalide is the starting-point, is both circuitous and costly.

In reply to a question from Mr. LEES, Dr. THORPE said that only primary nitriles reacted to form the imino-compounds; one of the two nitriles entering into the reaction must contain the group CH_2CN .

*205. "Note on the Anhydride of Phenylsuccinic Acid." By FRANCIS BERNHARD DEHN and JOCELYN FIELD THORPE.

The authors have investigated the anhydride of phenylsuccinic acid, and conclude that it exists in only one form, which melts at 53—54°. They have been unable to prepare the other form of the anhydride melting at 150° described by Bredt and Kallen, and by Wegscheider and Hecht, but by following the experimental details given by these investigators they have isolated an impure form of the acid which melts at this temperature. The authors have been unable to confirm the observation of Wegscheider and Hecht that the anhydride melting at 53—54° gradually passes into that melting at 150° when kept at the ordinary temperatures and also at 100°. They have kept specimens of the pure anhydride for several months under these conditions, and have observed no change.

*206. "Influence of Sodium Arsenate on the Fermentation of Glucose by Yeast-juice." (Preliminary Notice). By ARTHUR HARDEN and WILLIAM JOHN YOUNG.

It has been previously shown that when a soluble phosphate is added to yeast-juice containing glucose, the rate of fermentation is greatly increased (five to ten times), and proceeds at a gradually diminishing rate until an extra amount of carbon dioxide (equivalent, molecule for molecule, to the phosphate added) has been evolved. The rate then becomes equal to, or somewhat greater than, that of the original juice to which no addition has been made. The phosphate at the same time undergoes a change which renders it non-precipitable by magnesia mixture (*Proc. Roy. Soc.*, 1906, lxxvii., B, 405).

When an equivalent amount of arsenate is substituted for the phosphate a similar acceleration is produced, but the phenomena are somewhat different. The rate is greatly increased (eight to twelve times), but this high rate continues for a considerable time without change, until many times the equivalent of carbon dioxide has been evolved, and then falls gradually, the fermentation ceasing considerably before that of a sample of the same yeast-juice to which no addition of arsenate has been made.

An example is afforded by an experiment with the under-mentioned solutions:—

1. Twenty c.c. of yeast-juice + 5 c.c. water + 5 grms. glucose.

2. Twenty c.c. of yeast-juice + 5 c.c. 3M/10 di-sodium hydrogen arsenate + 5 grms. glucose.

The following numbers give the number of c.c. of carbon dioxide evolved during the time given in the first column:—

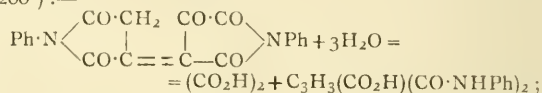
Time.	C.c. of CO ₂ .	
	Sol. I.	Sol. II.
1 hour	20·9	249·8
2 hours	41·2	491·5
5 "	99·5	797
6 "	118·1	831
7 "	136·2	848·8

At the end of seven hours, the rate per hour of Solution I was still 18 c.c. per hour, and that of Solution 2 had fallen from 249·8 to 14·8.

The rate attained and the duration of the fermentation vary both with the particular specimen of yeast-juice and with the amount of arsenate added, there being a certain optimum amount of arsenate for each sample of yeast-juice. The added arsenate remains precipitable by magnesia mixture after an equivalent of carbon dioxide has been evolved, and is also still in the same form when the fermentation ceases, so that in this respect it differs from the phosphate.

207. "Xanthoxalanil and its Analogues." By SIEGFRIED RUHEMANN.

When xanthoxalanil is acted on by caustic potash, it yields oxalic acid and dianilaconitic acids (m. p. 199—200°):—



the latter of which differs from the compound described by Michael (*Am. Chem. Journ.*, 1887, ix., 193), and, on hydrolysis with hydrochloric acid, furnishes aconitic acid. Xanthoxalo-m-xylidil, $\text{C}_{24}\text{H}_{20}\text{O}_5\text{N}_2$, similarly gives di-m-xylidil aconitic acid, melting at 196—197° with decomposition. Xanthoxalanil and its analogues are transformed into colourless substances on reduction with zinc dust and acetic acid. The compound (m. p. 160—161°) which is thus formed from xanthoxalo-m-xylidil, has the formula $\text{C}_{24}\text{H}_{26}\text{O}_5\text{N}_2$.

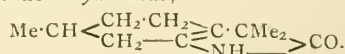
208. "Derivatives of Cyanodihydrocarvone and Cyano-carvomenthone." By ARTHUR LAPWORTH.

Cyanodihydrocarvone (*Trans.*, 1906, lxxix., 949) yields a cyanohydrin which is slowly hydrolysed by mineral acids, being finally transformed into 2-methyl-5-isopropenyl- Δ^2 -tetrahydroisophthalic acid. On reduction, the latter yields a mixture of isomeric 2-methyl-5-isopropenylhexahydroisophthalic acids, which, although still unsaturated, are not further reduced by sodium amalgam.

The addition compounds of cyanodihydrocarvone with hydrogen halides are well characterised substances which yield substitution products with bromine. The hydriodide may be reduced by zinc and methyl alcohol to cyano-carvomenthone, which may be converted by acids into carvo-methonecarboxylic acid, and by alkalis into carvotanacetone.

209. "Reactions involving the Addition of Hydrogen Cyanide to Carbon Compounds." Part VI. The Action of Potassium Cyanide on Pulegone." By REGINALD WILLIAM LANE CLARKE and ARTHUR LAPWORTH.

The compound $\text{C}_{11}\text{H}_{17}\text{ON}$, obtained by the action of potassium cyanide on pulegone, is easily converted into menthonecarboxylic acid (compare Hann and Lapworth, *Proc.*, 1904, xx., 54). The latter may be transformed into an unsaturated lactone, $\text{C}_{11}\text{H}_{16}\text{O}_2$, and from this, ammonia regenerates the initial substance $\text{C}_{11}\text{H}_{17}\text{ON}$, which is therefore not cyanomenthone, as was for a long time supposed, but the anhydramide,—



This is obtained in all cases where the isomeric cyanomenthone would be the normal product.

210. "The Influence of various Substituents on the Optical Activity of Tartramide." (Part II.). By PERCY FARADAY FRANKLAND and DOUGLAS FRANK TWISS.

In continuation of the previous work of P. F. Frankland and Slator (*Trans.*, 1903, lxxxiii., 1349), the authors have prepared and described the *n*- and isopropylamides the allylamide, the *n*- and isobutylamides, and the *n*-heptylamide of tartaric acid. The rotation of these compounds has been determined in pyridine, in methyl alcohol, and, when possible, also in aqueous solutions.

All the aliphatic amides have much lower molecular rotations than the aromatic amides. In the fatty amides of the normal series, the molecular rotation increases without exhibiting a maximum up to the heptyl term, which is as far as the series has yet been explored. The rotation of the benzylamide and furfurylamide follows closely on that of the heptylamide, there being a large gap between these and the true aromatic amides.

Special interest attaches to the lower rotation found for the allylamide than for the normal propylamide, as in general the appearance of a double bond in a compound is attended with a marked increase in the rotation.

211. "The Influence of various Substituents on the Optical Activity of Malamide." By PERCY FARADAY FRANKLAND and EDWARD DONE.

The authors described the preparation and properties of the methylamide, ethylamide, and isopropylamide, allylamide, and isobutylamide, *n*-heptylamide, piperidide, and phenylhydrazide of ordinary *l*-malic acid. The rotation was determined in pyridine, in methyl alcohol, and in glacial acetic acid solution.

The rotation is greatly influenced by the solvent. In pyridine solution, the amides of the normal series exhibit practically no change in molecular rotation from the methyl to the heptyl term. In methyl alcohol solution, on the other hand, there is a slight rise in the value of $[\alpha]_D$ between the methyl and heptyl terms, whilst in glacial acetic acid solution there is a slight decline over the same interval.

The allylamide has a markedly lower rotation than the normal propylamide.

The piperidide and phenylhydrazide have much lower rotations than any of the aliphatic amides; in fact, even lower than that of malamide itself.

Research Fund.

A meeting of the Research Fund Committee will be held in December. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, December 10th next.

ERRATA.—P. 227, col. 2, line 9 from bottom and in following cases, for "xanthdryl" read "xanthyl." P. 250, col. 2, lines 16 and 30, for "3-carboxylic" read "4-carboxylic."

Chromium Dioxide and the Constitution of Chromic Acid.—W. Manchot and R. Kraus.—The authors have prepared chromium dioxide by oxidising chromium oxide with gaseous oxygen. They obtained the former by precipitating the hydroxide with ammonia from chrome alum or chromium sulphate solution, and heating it in a test-tube until it suddenly glowed, and gave on cooling the green oxide. This was then heated to 240° and oxygen was passed over it for three or four hours. The dioxide was then cooled and decomposed again by heating, the oxygen being collected. The peroxide is a light very hygroscopic black powder; it gives up oxygen at a faint red heat, leaving the green oxide; with hydrochloric acid it gives off chlorine slowly, and it is gradually reduced by hydriodic acid. When pure it gives no chromic acid with cold water, but chromates are formed when it is warmed with alkalis. Probably it is a derivative of tetravalent chromium, O:Cr:O.—*Berichte*, xxxix., No. 13.

NOTICES OF BOOKS.

Paper Technology: an Elementary Manual on the Manufacture, Physical Qualities, and Chemical Constituents of Paper and of Paper-making Fibres. By R. W. SINDALL. London: Griffin and Co., Ltd. 1906.

THE author's perspective is set forth in the title and subtitle of this book, which are properly descriptive of its contents. The matter of the work being the substance of a course of lectures delivered in 1904-5, is, necessarily, in large part a compilation, but the original impress of the worker and master of the subject is uppermost throughout. As the title indicates, it is a treatise on Paper from the point of view of the user—and therefore buyer,—and the processes of manufacture are described only so far as it is necessary for the buyer to appreciate the dependence of quality upon the raw materials employed and the treatment by which they are converted into paper. Special chapters are devoted to Rag Papers, Esparto and Straw, Wood-pulp and Wood-pulp Papers, Packing and "Art" Papers, and they contain, not merely "stock" information, but a number of original observations which add considerably to the interest of these sections. Particularly we notice the critical discussion of the qualities and defects of the so-called "art" papers, excellently pointed by illustrations and by suggestions of the lines of investigation along which an ideal printing surface may be sought without sacrificing those qualities which condition permanence.

The sections devoted to the physical, mechanical, and chemical tests of the "expert" are very well handled, and the author's original grasp is evidenced by the inclusion of results of investigations which bring out the variation of the mechanical and physical constants of a given paper through the various stages of making, sizing, and finishing. The young student and the "practical" man will find that trouble has been taken to state the matter of this section in the clearest language; it is rounded off by a dictionary and glossary of terms used in the mill, the laboratory, and the trade.

The book commends itself by its title to a very wide circle of readers, and our judgment is that every section of workers in the industry of Paper will find that the author has identified himself by practical experience with their special needs and points of view, and they will derive both pleasure and profit from acquainting themselves with the results of this experience.

A History of Chemistry. By ERNST VON MEYER, Ph.D. Translated with the Author's Sanction by GEORGE MCGOWAN, Ph.D. Third English Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1906.

WHEN this History of Chemistry was first translated into English fifteen years ago, it was practically the only book of its scope which was at the disposal of English-speaking students; and now, although that state of affairs has been remedied, and the chemist has a choice both of complete histories of the science and also of monographs on special branches and periods, Prof. Ernst Meyer's History will still retain its place. The third English edition has been prepared from the third German edition, with various additions and alterations made by the translator with the author's sanction. The new matter which has been added deals chiefly with physical chemistry, the section on which has been much enlarged, as have also the chapters on agricultural and physiological chemistry, while there is an interesting section on the growth of chemical instruction, with special reference to Germany. Throughout the book there are also fresh biographical notices, and the record is brought down to the most recent date possible. The importance of the possession of a knowledge of the development of a science in order properly to appreciate its present standpoint is being constantly

more fully recognised, and an authoritative work such as this has a special value both for students and teachers.

Service Chemistry. By VIVIAN B. LEWES, F.I.C., F.C.S. and J. S. S. BRAME, F.C.S. Third Edition. London: Henry Glaisher. Greenwich: James Glaisher. 1906.

THIS manual of chemistry, which is intended more especially for the use of officers of the naval and military services, gives special prominence to such subjects as are likely to be of importance to its readers, and at the same time condenses, as far as possible, theoretical considerations. Thus the chemistry of fuels and explosives is discussed at greater length than is usual in a text-book of the size, and throughout the reader will find that he is specialising as far as is advisable; this does not, however, mean that general principles are neglected, but that practical applications are considered rather from a special than a general point of view, and there can be no doubt that this method of presenting the subject will be of great assistance to those for whom the book is intended. For the third edition the text has been carefully revised and extensive alterations made, so much so that the book has almost been re-written.

Manual of Chemistry. By W. SIMON, Ph.D., M.D. Eighth Edition. London: Baillière, Tindall, and Cox. 1906.

THE chapters on organic chemistry in this manual for the use of students of medicine, pharmacy, and dentistry have been entirely re-written, while additional space is given to dental metallurgy, and the whole of the text has been brought up to date. In its present form the book is a useful guide for dental and medical students, both as a text-book to supplement their lecture courses, as a work of reference, and for laboratory work, including both preparations and analysis. The valuable plates showing the colours of precipitates, indicators, &c., will be found useful as standards of comparison, and the copious lists of questions, if properly used, should help to fix the student's knowledge. Physiological chemistry is well treated, and the section on organic chemistry also gives a clear review of the essentials of the subject.

Die Untersuchung des Erdöles und seiner Produkte. ("The Examination of Petroleum and its Products"). By M. A. RAKUSIN. Braunschweig: Friedrich Vieweg und Sohn. 1906.

THIS book discusses practical methods of testing naphtha, with special reference to the recommendations of the Baku and St. Petersburg Commissions for the establishment of standards for the testing of naphtha products. It aims at giving a complete account of the physico-chemical methods of examining mineral oils as far as they are of scientific or practical interest, while synthetic methods of preparation and the geological aspect of the subject are not touched upon. Much of the author's own work is described in the text—not, however, to the exclusion of that of other investigators. Many tables of interest in the testing of mineral oils are included—such as, for example, those of the specific gravities of kerosene and naphtha residues at different temperatures, and full practical descriptions of the necessary experimental work are given. The various methods of storing mineral oils are illustrated and discussed. The weighing of liquids in stationary holders by means of the pneumatic reservoir balance of Sacharoff is considered at length, its possible technical importance being fully recognised. The author has been at pains to overlook no question which comes within his province, and the outcome of his labours is a complete and comprehensive account of scientific and technical methods of testing naphtha products.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 19, November 5, 1906.

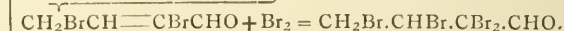
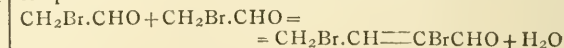
Alcoholysis of Fatty Bodies.—A. Haller.—The author's researches prove—(1) That all the glycerides can be subjected to alcoholysis, and that those of low molecular weight are more easily decomposed than the higher glycerides; (2) that all the fatty bodies soluble in alcohol alcoholyse more easily than those which are insoluble; (3) that alcoholysis is facilitated when the operation takes place in the medium of a solvent of the fatty body; (4) that the transformation of fatty matters into glycerin and ether salts constitutes a very practical method for the preparation of a certain number of these ethers and also a new method of qualitative analysis of the same substances; (5) that the operation of alcoholysis takes place at a relatively high temperature, and in presence of a little acid allows certain bodies which are only present in natural products in minute quantities to be recognised by their perfume.

Conditions of Precipitation and Re-dissolving of Metallic Sulphides.—H. Baubigny.—The author performs a series of experiments on the subject of the precipitation and re-dissolving of a number of metallic sulphides, and finds that his conclusions are identical with those of MM. Bruni and Padva.

Gases evolved during the Action of Potash on Tantalite.—C. Chabré and F. Levallois.—When tantalite is heated alone a slight evolution of gas takes place, the composition being—CO₂, 84 per cent; N, 12.4 per cent; O, 3.1 per cent; but when it is fused with four times its weight of potash *in vacuo* a copious evolution of gas takes place, the composition in this case being—H, 93.2 per cent, N, 4.6 per cent; and O, 1.2 per cent. Both substances are chemically pure. The authors explain this reaction as follows:—It must be admitted that the potash is substituted for the protoxide of iron in the mineral; then that this iron protoxide reduces the potassium hydrate, giving water, hydrogen, and sesquioxide of iron: $2\text{Ta}_2\text{O}_5 \cdot \text{FeO} + 4\text{KOH} = 4\text{TaO}_3\text{K} + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} + \text{H}_2$.

Selenium.—Oechsner de Coninck.—The selenium which is prepared from the sulphoxide appears to be of a stable variety, and it is interesting to note that the selenium which enters into the compound SeSO₃ in a certain physical form can be taken away from this compound in a totally different form.

Chloruration of Paraldehyde and Butyric Chloral.—P. Freundler.—The author investigates the difference between the action of bromine and chlorine on paraldehyde. He finds that the chloruration can only be effected at ordinary temperatures and under the conditions in which acetic aldehyde and chloroacetic aldehyde are condensed under the influence of hydrochloric acid to form α -chloro-crotonic aldehyde. On the contrary, the bromuration of paraldehyde takes place almost integrally at 0°, *i.e.*, at a temperature below that of crotonisation:—



Chloral and bromal appear to be able to be acetalised in the same way as butyric chloral. These various acetals, the author hopes, will enable him to effect some interesting syntheses.

Phenyl Migration.—M. Tiffeneau.

Constitutional Formula of certain Dimethyl-anthracenes.—James Lavaux.—In order to control certain deductions regarding the constitutional formula of dimethylanthracenes, the author oxidises β -dimethylanthracene, first to dimethylanthraquinone, then to methylanthraquinone carbonic acid, which by means of zinc and ammonia he reduces into methylanthracene carbonic acid, and finally, after distillation with soda-lime, obtains β -methylanthracene. This and another experiment described in detail are enough to establish the constitution of the bodies.

MISCELLANEOUS.

Dimethylglyoxim: a New Reagent for Nickel.— α -Dimethylglyoxim (see C. Schramm, *Ber.*, 1883, p. 180), $\text{CH}_3\text{C}(\text{N} \cdot \text{OH})\text{C}(\text{N} \cdot \text{OH})\text{CH}_3$, forms white crystals melting at 240°C . sparingly soluble in water, but dissolving freely in alcohol and ether. L. Tschugaeff (*Ber.*, 1905, p. 2520) discovered accidentally whilst investigating the properties of some complex substances that dimethylglyoxim is an extremely sensitive reagent with respect to nickel. The solution to be tested is mixed with ammonia or sodium acetate in excess, a little powdered dimethylglyoxim is then added, and the mixture made to boil. In the presence of nickel a beautiful scarlet-red precipitate forms either at once or when the solution has cooled, according to the proportion of nickel present. The dioxim which separates out during the process of cooling acquires likewise a distinct pink tint through the influence of the nickel. The reagent is, according to E. Tschugaeff, sensitive enough to indicate the presence of 1 part of nickel in 400,000 parts of water. When the simultaneous presence of cobalt is suspected, especially when it is required to test salts of cobalt for absence of nickel, the method has to be applied in a slightly modified form, since cobalt forms a brown compound with the reagent. In this case the test solution should be shaken up repeatedly with a large excess of ammonia, which gives rise to the formation of complex cobaltamines, and the resulting solution should be tested for nickel. On filtering the solution after the addition of the reagent the red nickel compound remains upon the filter, after drying it dissolves in a hot mixture of chloroform and alcohol, and after the evaporation of the solvent remains in the form of microcrystalline spiculae. It is claimed that nickel may thus be distinguished in the presence of 5000 times the quantity of cobalt.—*Merck's Annual Report*, for 1905.

MEETINGS FOR THE WEEK.

- MONDAY, Dec. 3rd.**—Royal Institution, 5. General Monthly Meeting.
Society of Arts, 8. (Cantor Lectures). "Artificial Fertilisers—their Nature and Functions," by A. D. Hall.
Society of Chemical Industry, 8. "Direct Estimation of Antimony," by H. W. Rowell.
"Bacterial Method of Investigating Disinfectants," by M. Wynter Blyth. "Detannisation of Solutions in the Analysis of Tanning Materials," by J. G. Parker and H. G. Bennett.
- TUESDAY, 4th.**—Society of Arts, 4.30. "The Cape to Cairo Railway," by The Hon. Sir Lewis Lloyd Michell.
- WEDNESDAY, 5th.**—Society of Arts, 8. "The Metric System," by Col Sir Charles M. Watson, K.C.M.G., &c.
Society of Public Analysts, 8. "Amount of Calcium Oxalate in the Ash of Cinnamon and Cassia Barks," by J. Hendrick. "Estimation of Preservatives in Milk," by H. S. Shrewsbury. "Fractional Distillation by Steam Vapour," by H. Hardy and B. Richens. "Estimation of Mineral Acid in Vinegar," by P. Schidrowitz.
- THURSDAY, 6th**—Chemical, 8.30. "Liquid Volume of a Dissolved Substance," by J. S. Lumsden. "Some Derivatives of Benzophenone—Synthesis of Substances occurring in Coco-bark," by W. H. Perkin, jun., and R. Robinson. "Synthesis of Terebic, Terpenylic, and Homoterpenylic Acids," by J. L. Simonsen.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Methyl Butadiene.—Can any reader give particulars of the synthesis of methyl butadiene, $\text{CH}_3\text{CMe} \cdot \text{CH} \cdot \text{CH}_2$?—M. H.

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THE CHEMICAL NEWS.

VOL. XCIV., No. 2454.

ISOMORPHOUS CRYSTALS OF THE NITRATES OF BARIUM AND LEAD.

By P. GAUBERT.

A CRYSTAL in the course of growth can sometimes be coupled with a greater or smaller amount of another crystalline substance in solution in its mother-liquor, and, if this is a colouring matter, the faces belonging to the different forms do not always have the same coefficient of absorption. Hydrated phthalic acid, coloured by the aniline dyes, furnishes an excellent example of this property.

I have been led to enquire whether a phenomenon of the same nature is not produced in isomorphous mixtures. To this end I have experimented on the nitrates of barium and of lead, the mixed crystals of which have been the object of many discussions from other points of view.

It is known that these two substances, dissolved individually or together, always give by cooling a pure boiling solution, octahedra, and by slow evaporation at the ordinary temperature, especially if the solution be acidified with nitric acid, cubic octahedra with several other slightly developed faces, in particular the pentagonal dodecahedral.

I have before demonstrated that the crystals of these nitrates, and above all those of lead nitrate, crystallising in a mother-liquor containing methylene blue, absorb far more of the colouring matter by the cubic faces than by the other faces, and it is this fact that led me to experiment on the cubic nitrates amongst the isomorphous bodies. I sought to determine if the octahedral faces and the cubic faces of the crystals of barium nitrate absorb the same quantity of lead nitrate, dissolved in small quantity in the mother-liquor, and reciprocally.

In one series of experiments 500 grms. of barium nitrate, and 10 grms. of lead nitrate were dissolved, each time in water, and the solution saturated at the ordinary temperature was slowly evaporated at 18° to 25°. When a sufficient quantity of crystals had been deposited, a gm. of the substance was detached from the pyramids corresponding to the octahedral faces, and another gm. from those of the cubic formation.

This preparation obviously demands much care and patience. The estimation of the lead by a colorimetric method shows that the amounts of the crystals with octahedral faces contain more lead than the cubic crystals. The determinations were repeated several times, and the results were always in agreement.

The ratios of the quantities of lead were found approximately equal to 4 : 3, 5 : 3, 5 : 4, 9 : 8. They differed a little among themselves, the quantities of lead nitrate crystallising with barium nitrate varying with the temperature, and their estimation being difficult, but they indicated sufficiently well the nature of the phenomenon.

I took the precaution of using transparent crystals to eliminate the error due to inclusions of the mother-liquor upon the two classes of crystals.

Similar estimations were made with crystals of lead nitrate obtained by slow evaporation of a solution containing a small quantity of baryta and of nitric acid. It was still the octahedral faces which absorbed more of the barium nitrate than the cubic.

These results explain the complexity of the optical properties of the cubic nitrates. In the crystals of lead nitrate containing a small quantity of barium nitrate, the axes corresponding to each class of face have a particular double refraction (F. Klocke, R. Brauns, J. Morel, &c.)

The pyramids with the octahedral faces are much more doubly refracting than the cubic, often singly refracting, and less so than those of the pentagonal dodecahedral formation; it is also known that the double refraction increases with the amount of barium nitrate contained in the crystal. Consequently, my experiments show that if the various axes have not the same double refraction, it is because they have not the same chemical composition.

To sum up, a crystal of lead nitrate containing barium nitrate, and *vice versa*, is not homogeneous, in spite of its transparency and clearness; it is built up by the grouping of pyramids of which the composition varies with the nature of the faces to which they correspond. The same structure is observed in certain minerals of the volcanic rocks, in explanation of which numerous theories have been advanced. My experiments show that this structure should be considered as the primary cause; it is fixed before the first appearing of the crystallisation.—*Comptes Rendus*, cxliii., No. 21, p. 776.

CONTRIBUTION TO THE STUDY OF PER-SALTS.*

By Prof. E. PINERUA ALVAREZ.

THE per-salts obtained and studied by us are the pernitrates, perphosphates, perarsenates, pertungstates, perphosphotungstates. They are all derived from the corresponding peroxidised acids, in which part of the oxygen is loosely combined with the rest of the molecule, a slight elevation of temperature or the action of acidified water being sufficient to decompose these salts, setting free all the oxygen which we can call displaceable, and which unites with the water, if the temperature is low, to produce hydrogen peroxide; hence these are hydroperoxylic salts.

They are all easily obtained by the action of sodium dioxide on the alkaline salts of nitric, phosphoric, arsenic, tungstic, and phosphotungstic acids.

We obtained the pernitrate by dissolving 100 grms. of nitre in a mixture of 2000 grms. of water and 1800 or alcohol at 98°, then cooling the vessel containing the solution with ice and salt; finally, 160 grms. sodium dioxide is added by degrees, part of the salt produced is precipitated by the action of 1800 grms. absolute alcohol, the liquid is rapidly filtered on the pump, carefully washed with anhydrous alcohol, the product recovered from the filter, and finally dried in the vacuum and in presence of phosphorus anhydride.

The filtered liquids on evaporation give the greater part of the salt.

The method of procedure followed by us in order to obtain the other per-salts is exactly the same.

The quantities of the substances used are as follows :—

Sodium perphosphate—	Grms.
Di-sodium phosphate	50
Alcohol	3000
Water	3000
Sodium dioxide	70
Sodium perarsenate—	
Di-sodium arseniate	50
Water	2000
Alcohol	2000
Sodium dioxide	100
Sodium pertungstate—	
Sodium tungstate	50
Alcohol	1000
Water	1000
Sodium dioxide	90

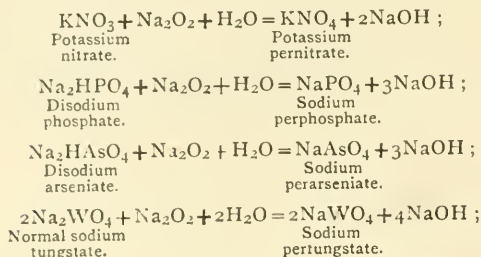
* Note presented at the Sixth International Congress of Applied Chemistry, held at Rome, 1906.

Sodium phosphopertungstate—

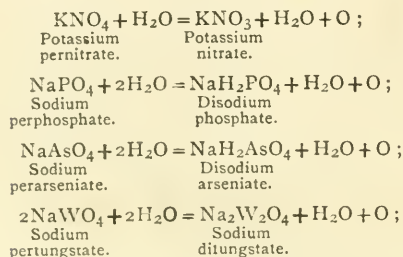
Phosphotungstic acid	20
Water	750
Alcohol	750
Sodium dioxide	80

In each case the precipitation was effected with anhydrous ethyl alcohol, and the precipitate washed and dried as already described. The filtration liquids by spontaneous evaporation gave us the greater part of the crystallised salts.

The reactions of formation are as follows :—



The reactions of decomposition by water are :—



The quantities of oxygen determined by experiment represent the former equalities.

If the water be strongly acidified, we find in the second members of these equations the corresponding sodium bisulphate, and free nitric, phosphoric, arsenic, and tungstic acids.

All the alkaline per-salts quoted are solids, and of a white colour. They occur also in amorphous and crystalline forms.

The amorphous varieties, obtained by precipitation with alcohol, contained varying quantities of the hydrate of sodium dioxide, which almost completely veil the true chemical properties of these per-salts.

I have even observed this in many specimens of commercial amorphous perborates, which have a strongly alkaline reaction, due principally to the hydrate of the dioxides, which makes them caustic and unsuitable for use in medicine.

On the other hand, the crystallised salts, after being carefully washed and dried *in vacuo*, are neutral, and their chemical reactions are very different from those of the amorphous varieties.

We will consider here the chief chemical properties of the per-salts quoted, and those of the hydrate of the dioxide, in order to compare them with those exhibited by the amorphous.

I. With lead acetate all the crystallised per-salts give a white precipitate of the lead per-salt, soluble in nitric acid with brisk effervescence.

The amorphous per-salts give a red precipitate of sodium and lead orthophosphate, which with nitric acid gives a residue of PbO_2 .

The hydrate of the dioxide gives the same red precipitate.

II. With silver nitrate all the crystallised per-salts give a white precipitate, but the silver compounds of these

peroxidised acids are so unstable that after a short time they turn grey or yellow, with liberation of oxygen.

The amorphous per-salts all produce with this reagent a grey or black precipitate, which is a mixture of silver and the peroxide of the same metal.

The hydrate of the peroxide reacts similarly to the amorphous salts.

III. With mercurous nitrate the white precipitate formed by the crystallised per-salts decomposes very rapidly, and becomes blackish grey or brown (perphosphate). The amorphous per-salts, like the hydrate of sodium dioxide, NaO.OH , give immediately a black precipitate.

IV. With mercuric chloride all the crystallised per-salts form a very intense red precipitate, soluble with effervescence in hydrochloric acid.

The amorphous per-salts produce with mercuric chloride a yellow-red precipitate like that of the hydrate of sodium peroxide.

V. With copper sulphate the crystallised per-salts give a blue precipitate of the cupric per-salt.

The amorphous per-salts give with it a yellow-green basic salt, and with a great excess of per-salt and heat it becomes black.

VI. With the sulphates of zinc and cadmium both the crystallised and amorphous per-salts give a white precipitate.

VII. With a solution of bismuth nitrate neutralised to cloudiness, the crystallised per-salts give a white crystalline precipitate.

The amorphous per-salts give rise to a yellow-red precipitate, which is the hydrate of bismuth dioxide, BiO(OH)_2 . This last reaction is identical with that of the hydrate of sodium dioxide with the same bismuthic salt.

VIII. With gold chloride the crystallised per-salts produce only a slight effervescence, due to the oxygen set free by hydrolysis of the per-salt.

The amorphous per-salts give rise first to a blue liquid due to the reduction of the auric hydrate to aurous, and then a precipitate of metallic gold.

The hydrate of the dioxide gives rise to the auric hydrate, which hydrogen peroxide reduces to the aurous hydrate (blue), and finally to metallic gold.

IX. With manganous chloride and sulphate, the crystallised per-salts give a very stable pink precipitate of the manganous per-salt, soluble with effervescence in hydrochloric acid.

The amorphous variety produces a purple or brown deposit of manganic hydrate.

The hydrate of the dioxide produces the same reaction.

X. With the sulphate and chloride of nickel the crystallised per-salts give a whitish green precipitate of the nickel per-salt. The amorphous salts give a precipitate of the basic salt, like the hydrate of sodium dioxide.

XI. With cobaltous nitrate and chloride the crystallised per-salts give precipitates of a beautiful pink colour, which are the cobaltous per-salts.

The amorphous per-salts produce first a yellowish green precipitate, which finally becomes the deep brown of cobaltic hydrate. The hydrate of sodium dioxide produces the latter reaction.

XII. With ferrous sulphate all the crystallised per-salts give a green or blue-green precipitate, which with the pernitrate becomes so intense that it appears black.

The amorphous salts form, like the hydrate of the dioxide, a red precipitate of ferric hydrate.

XIII. With ferric chloride the crystallised per-salts, as well as the amorphous, give a red precipitate of ferric hydrate.

XIV. With the chlorides of calcium, barium, and strontium, all the crystallised per-salts give a white crystalline precipitate of the calcium, barium, and strontium per-salts.

XV. The crystallised per-salts added to a solution of potassium iodide, to which a few drops of sulphuric acid are then added, set free the iodine, and the liquid becomes yellowish red.

The amorphous per-salts, as well as the hydrate of sodium dioxide, present the same phenomenon, but with greater intensity.

The pernitrites with ferrous sulphate and sulphuric acid produce a brisk effervescence due to evolution of oxygen, and assume the characteristic colour of the nitrates.

The perphosphates and perselenates give precipitates with the magnesium and molybdate mixture.

Finally, if to 0.5 grm. of sodium pertungstate or phosphertungstate 10 c.c. distilled water be added, and 5 c.c. hydrochloric acid, an abundant evolution of oxygen is at once manifested. On boiling the mixture in a little glass vessel an abundant yellow precipitate of metatungstic acid is preceived after some time, and if stannous chloride be then added the liquid acquires a blue colour, and the blue oxide of tungsten is precipitated.

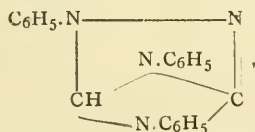
It is obvious that these salts might play an important part in medicine, in the arts and industries, and in chemical analysis, &c.

The pernitrites, for example, which give through the action of heat from 15 to 16 per cent of oxygen, in addition to what they yield as nitrates, are very readily ignited, and therefore of service in the manufacture of explosives.

The perphosphates, which liberate by the action of water from 13 to 14 per cent of oxygen, can be of signal use in medicine.

NITRON: A NEW REAGENT FOR NITRIC ACID.

NITRON, or 1.4-diphenyl-3.5-endanilo-dihydro-triazol,—



is a base consisting of lustrous yellow leaves or an amorphous powder. The preparation fuses and decomposes at 189° C.; it dissolves in alcohol, benzol, chloroform, acetone, and acetic ether, with difficulty in ether, but is insoluble in water. The nitrate of this base $\text{C}_{20}\text{H}_{16}\text{N}_4\text{---HNO}_3$, being likewise difficultly soluble in water (at 0° C. to the extent of 1 : 80,000, at ordinary temperature to the extent of 1 : 60000), has suggested itself to M. Busch (*Ber.*, 1905, p. 861), as a practical medium for the identification and quantitative determination of nitric acid and nitrates. According to the investigations of A. Gutbier (*Zeit. Angewandte Chemie*, 1905, No. 13, p. 494), the difficulty with which the salt dissolves is likewise of special value as a means of qualitatively demonstrating in water the presence of nitrates, which may also be determined quantitatively with sufficient accuracy by means of nitron. The reagent consists of a solution of 10 grms. of nitron in 90 grms. of 5 per cent acetic acid. The addition to this of a neutral solution of nitrates or one feebly acidulated with sulphuric acid, either immediately gives rise to a white crystalline precipitate of nitron nitrate depending in quantity upon that of nitrates present, or the nitron nitrate crystallises out quantitatively in the course of a few hours. After washing with a small quantity of cold water the nitron nitrate may be weighed upon a weighed filter or in a Neubauer crucible.

The quantitative analysis is carried out in the following manner:—

Dissolve the substance containing about 0.1 grm. of nitric acid in 80 to 100 c.c. water, add 10 drops of dilute sulphuric acid, heat till near boiling point, and add 10 to 12 c.c. nitron acetate solution. Stand the vessel for one

and a-half to two hours in ice water, separate the resulting precipitate by aspiration in a Neubauer crucible, rinsing with the filtrate, and having carried the separation as far as possible, wash with 10 to 12 c.c. ice water. The washing water is added in small portions, time being allowed each time for its complete aspiration. Dry the precipitate at 110° C., when the point of constancy of weight will be found to be attained in three-quarters of an hour.

The calculation conforms to the formula $\text{C}_{20}\text{H}_{16}\text{N}_4\text{---HNO}_3$, i.e. the resulting weight of nitron nitrate $W \times \frac{175}{275}$ is a measure of the quantity of nitric acid present. The high molecular weight of nitron nitrate endows the method with a special advantage, since any differences of observation which may present themselves become reduced to one-sixth in the evaluation of the nitric acid.—*Merck's Annual Report* for 1905.

A REVISION OF THE ATOMIC WEIGHT OF BROMINE.*

By GREGORY PAUL BAXTER.

(Concluded from p. 262).

The Ratio of Silver Bromide to Silver Chloride.

THE ratio of silver bromide to silver chloride was determined much as described in previous papers upon the atomic weight of iodine (Baxter, *Proc. Am. Acad. Arts Sci.*, 1904, xl., 432, and 1905, xli., 75; *Journ. Am. Chem. Soc.*, 1905, xxvii., 876). Pure silver bromide was prepared by precipitation of silver nitrate with an excess of ammonium bromide. The silver employed was purified either by precipitation as chloride and reduction with invert sugar, or by electrolysis, or by precipitation with ammonium formate. The metal was then fused before a blowpipe upon a crucible of the purest lime, and the buttons were thoroughly cleansed with nitric acid. No further purification was considered necessary, since the weight of the metal was of no consequence.

After the silver bromide had been washed by decantation with water, in some cases it was collected in a Gooch crucible in which a disk of filter-paper was employed instead of asbestos, and after drying at 100° it was carefully separated from the filter-paper. In other cases the precipitate was transferred to a platinum dish, and was drained with a platinum reverse filter with a disk of filter-paper (Cooke, *Proc. Am. Acad. Arts Sci.*, xii., 121). In still others a platinum Gooch crucible with small holes was found to be sufficiently effective as a filtering medium without the use of either asbestos or filter-paper.

Before being weighed the silver bromide was fused in a current of air saturated with bromine in a weighed quartz crucible. The air was purified by passing successively over beads moistened with silver nitrate solution, over sodium carbonate, and finally over concentrated sulphuric acid which had been heated to its boiling-point with a small quantity of re-crystallised potassium dichromate to eliminate volatile and oxidisable impurities. The air was then passed through dry bromine in a small bulb. This apparatus was constructed entirely of glass with ground joints. The tube which conducted the gases into the crucible passed through a Rose crucible cover of glazed porcelain in all experiments except Analysis 28 to 31, in which a quartz cover was employed. The quartz crucibles were always contained in large porcelain crucibles while being heated. They remained almost absolutely constant in weight during the experiments. The bromine was in each case a portion of the sample from which the silver bromide had been made.

Next the bromide was heated barely to fusion in a slow current of chlorine, generated by the action of hydrochloric

* From the *Journal of the American Chemical Society*, xxviii., No. 10

TABLE I.—THE ATOMIC WEIGHT OF BROMINE (SERIES I.).
(Ag : AgBr. Ag = 107.930).

No. of analysis.	Sample of silver.	Sample of bromine.	Weight of silver in vacuum (grms.).	Weight of silver bromide in vacuum (grms.).	Loss on fusion in bromine (grm.).	Weight of asbestos (grm.).	Dissolved silver bromide (grm.).	Corrected weight of silver bromide (grms.).	Ratio, Ag : AgBr.	Atomic weight of bromine.
1.	A	II.	4.71853	8.21362	0.00027	0.00007	0.00021	8.21363	57.4476	79.946
2.	B	II.	5.01725	8.73387	0.00020	0.00019	0.00007	8.73393	57.4455	79.952
3.	A	II.	5.96818	10.38799	0.00023	0.00034	0.00122	10.38932	57.4453	79.953
4.	C	II.	5.62992	9.80000	0.00017	0.00039	0.00017	9.80039	57.4459	79.951
Average									57.4461	79.950
5.	A	IV.	8.13612	14.16265	0.00002	0.00047	0.00024	14.16334	57.4449	79.954
6.	C	IV.	5.07238	8.82932	0.00013	0.00043	0.00035	8.82997	57.4451	79.954
7.	B	IV.	4.80711	8.36838	0.00015(a)	0.00000	0.00004	8.36827	57.4445	79.956
Average									57.4448	79.955
8.	C	V.	4.27279	7.43771	0.00010(a)	0.00009	0.00007	7.43776	57.4473	79.947
9.	A	V.	5.86115	10.20299	0.00007(a)	0.00004	0.00003	10.20299	57.4454	79.953
10.	B	V.	7.91425	13.77735	0.00010	0.00010	0.00001	13.77736	57.4439	79.958
11.	D	V.	6.40765	11.15461	0.00000	0.00006	0.00001	11.15468	57.4436	79.959
12.	D	V.	6.38180	11.10942	0.00025	0.00012	0.00001	11.10930	57.4456	79.952
13.	D	V.	6.23696	10.85722	0.00005	0.00004	0.00001	10.85722	57.4453	79.953
Average									57.4452	79.953
14.	E	I.	9.18778	15.99383	0.00014	0.00019	0.00004	15.99392	57.4455	79.953
15.	E	I.	8.01261	13.94828	0.00018	0.00009	0.00007	13.94826	57.4452	79.953
16.	E	I.	10.48638	18.25467	0.00025(a)	0.00007	0.00001	18.25452	57.4454	79.953
Average									57.4454	79.953
17.	E	III.	8.59260	14.95790	0.00014	0.00016	0.00005	14.95797	57.4450	79.954
18.	E	III.	8.97307	15.62013	0.00004	0.00007	0.00006	15.62022	57.4452	79.953
Average									57.4451	79.954
Total			121.67653					211.81305	57.4452	79.953
Average of all eighteen determinations..									57.4453	79.953
Average of last seven determinations ..									57.4453	79.953

(a) Fusion in bromine lost after the salt had been fused in air.

acid upon manganese dioxide, and dried by means of concentrated sulphuric acid. The apparatus for this purpose also was constructed wholly of glass. When the bromine was apparently completely displaced, the silver chloride was heated in the air for a few minutes to expel dissolved chlorine, and then was cooled and weighed. A repetition of the heating in chlorine seldom affected the weight of the salt more than a few hundredths of a m.grm., although occasionally a third heating was necessary to effect this result.

That no loss of silver chloride by volatilisation took place is certain for two reasons. In the first place the cover of the crucible and the delivery tube for the bromine when rinsed with ammonia and the solution treated with a slight excess of hydrochloric acid gave no visible opalescence in the nephelometer. In the second place the weight of the chloride became constant without difficulty. It has already been shown that silver chloride which has been fused in chlorine, if subsequently heated in air, retains no excess of chlorine (Baxter, *Proc. Am. Acad. Arts Sci.*, 1904, xl., 432; *Journ. Am. Chem. Soc.*, 1904, xxvi., 1591; Richards and Wells, Publications of the Carnegie Institution, No. 28, p. 59).

The following vacuum corrections were applied:—Silver bromide, + 0.000041; silver chloride, + 0.000071. (Richards and Stull have found the density of fused silver chloride to be 5.56). The atomic weight of chlorine referred to silver 107.930 is assumed to be 35.473.

Aside from the close agreement of all the results of Series I., the fact is to be emphasised that of the last seven analyses, which were consecutive, only two differ from the average of the series, 79.953, by as much as one one-thousandth of a unit. Furthermore, there is no evidence of any dissimilarity in the different preparations of bromine. Material which has received only two distillations from a bromide gives value no lower than bromine which has been thus treated four times. The various specimens of silver also show no difference in purity.

In the case of Series II., the extreme variation of the results is only four-thousandths of a unit, and only one of the thirteen experiments yielded a value which differs from the average by more than one-thousandth of a unit.

Finally, the difference between the averages of Series I. and II. is only seven ten-thousandths of a unit. It is extremely unlikely that constant errors could have affected both series equally, so that this striking agreement is strong proof that both series are free from such errors.

It has already been pointed out that the average of Stas's syntheses, 79.954, probably represents with considerable accuracy the atomic weight of bromine, and that certainly his determinations are more accurate than those of later experimenters. His syntheses are few in number, however, and differ among themselves by several thousandths of a unit, so that they do not define within this amount the constant in question. Their average, however, confirms the value obtained in this paper. From

all the experiments here described the number 79.953 seems to be the most probable value for the atomic weight of bromine if the atomic weight of silver is assumed to be 107.930.

TABLE II.—The Atomic Weight of Bromine (Series II.).

		AgBr : AgCl.			
		(Ag = 107.930. Cl = 35.473).			
Number of analysis.	Sample of bromine.	Weight of silver bromide in vacuum. Grms.	Weight of silver chloride in vacuum. Grms.	Ratio. AgBr : AgCl.	Atomic weight of bromine.
19.	II.	8.03979	6.13642	131.0176	79.953
20.	II.	8.57738	6.54677	131.0170	79.952
21.	II.	13.15698	10.04221	131.0168	79.952
Average ..		..	..	131.0171	79.952
22.	IV.	12.71403	9.70413	131.0167	79.952
23.	IV.	13.96784	10.66116	131.0162	79.951
Average ..		..	..	131.0164	79.952
24.	V.	13.08168	9.98469	131.0174	79.953
25.	V.	12.52604	9.56059	131.0175	79.953
26.	V.	11.11984	8.48733	131.0170	79.952
27.	V.	8.82272	6.73402	131.0172	79.953
Average ..		..	..	131.0173	79.953
28.	I.	11.93192	9.10721	131.0162	79.951
29.	I.	12.53547	9.56767	131.0190	79.955
Average ..		..	..	131.0176	79.953
30.	III.	17.15021	13.09009	131.0167	79.952
31.	III.	10.31852	7.87572	131.0168	79.952
Average ..		..	..	131.0168	79.952
Total ..		153.94242	117.49801	131.0170	79.952
Average of all thirteen experiments				131.0171	79.952
Average of Series I. and II.				..	79.953

In conclusion, attention may be called to the fact that a diminution in the atomic weight of bromine raises slightly all atomic weights resulting from the analysis of metallic bromides by precipitation with silver.

I am deeply indebted to the Carnegie Institution of Washington and to the Cyrus M. Warren Fund for Research in Harvard University for assistance in pursuing this investigation.

THE ESTIMATION OF FLUORINE IODOMETRICALLY.

By ALBERT HILEMAN.

It is obvious that the reaction by which fluosilicic acid liberates iodine from a mixture of potassium iodide and potassium iodate may be turned to account in the analysis of fluorides as well as in the determination of fluosilicic acid provided the course of action is regular.

Upon testing the action of hydrofluosilicic acid upon the iodide-iodate mixture, it was found that, while iodine is liberated freely in the cold, a complete reaction was not obtained in the course of several hours—the amount of iodine liberated indicating that an acid other than fluosilicic acid as a unit was acting. It appeared, however, that on boiling the mixture nearly one equivalent of iodine is

liberated for every equivalent of fluorine present as fluosilicic or hydrofluoric acid. The reaction may be written $5\text{KI} + \text{KIO}_3 + \text{H}_2\text{SiF}_6 \rightarrow 6\text{KF} + 6\text{I} + \text{SiO}_2 - \text{H}_2\text{O}$.

To the fluosilicic acid in a flask was added a neutral solution of potassium iodide and iodate in excess, and the flask closed with a glass stopper fitted with a trap containing a solution of potassium iodide to retained volatilised iodine. The solution in the flask was heated to boiling, then cooled, and, together with the contents of the trap, titrated with a standard solution of thiosulphate.

In Section A of Table I. are given the results obtained with a solution of commercial fluosilicic acid. Titrations with sodium hydroxide and comparative iodometric determinations are given. In Section B of Table I. the results of similar experiments with fluosilicic acid made by the action of hydrofluoric acid on an excess of silica are given.

The indications by the iodometric method are lower than those of the alkalimetric method of titration by about 0.0008 grm., on the average. This fact would indicate that the iodine liberated does not quite correspond to the complete hydrolysis of fluosilicic acid indicated by the theoretical equation.

Likewise Table II. shows the results obtained by applying the iodometric method to the silicon fluoride eliminated from calcium fluoride, according to the method proposed in a previous paper (*Am. Journ. Sci.*, xxii., 329).

TABLE I.

H_2SiF_6 .	Standard NaOH_3 .	Standard $\text{Na}_2\text{S}_2\text{O}_8$.	Fluorine found.
	(1 c.c. = 0.005137 of fluorine).	A. (1 c.c. = 0.002335 of fluorine).	
C.c.	C.c.	C.c.	Grm.
25	10.82	—	0.0556
25	10.87	—	0.0559
25	10.83	—	0.0557
25	—	23.54	0.0549
25	—	23.52	0.0049
25	—	23.48	0.0548
25	—	23.50	0.0548
25	—	23.45	0.0548
25	—	23.48	0.0548
	(1 c.c. = 0.005137 of fluorine).	B. (1 c.c. = 0.002441 of fluorine).	
25	9.08	—	0.0466
25	9.05	—	0.0464
25	9.05	—	0.0464
25	—	18.78	0.0458
25	—	18.80	0.0459

Calcium fluoride was treated in the apparatus figured by the method described, the silicon fluoride was absorbed in water, and after separating the mercury used in the apparatus by means of a separating funnel, the iodide-iodate mixture was added to the solution, and the iodine liberated was titrated by sodium thiosulphate.

TABLE II.

CaF_2 .	(1 c.c. = 0.002335). $\text{Na}_2\text{S}_2\text{O}_8$.	Fluorine.		
		Theory.	Found.	Error.
Grm.				
0.2500	51.35	0.1216	0.1199	0.0017
0.2300	46.75	0.1119	0.1091	0.0028
0.2300	47.15	0.1119	0.1100	0.0019
NaF .				
0.2000	38.50	0.0903	0.0899	0.0014

The average error of -0.0019 grm. is considerably greater than that of the alkalimetric method, 0.0008 grm. It appears, therefore, that, while the iodometric method of determining fluorine in fluorides may in special cases present some advantages, it does not equal in accuracy the alkalimetric method when it is properly conducted.—*American Journal of Science*, [4], xxii., p. 383.

THE USE OF THE ROTATING CATHODE FOR THE ESTIMATION OF CADMIUM TAKEN AS THE SULPHATE.*

By CHARLES P. FLORA.

IN a recent paper from this laboratory (Gooch and Medway, *Am. Journ. Sci.*, 1903, [4], 320) has been described the application of the rotating cathode to the rapid estimation of copper, silver, and nickel; and, in a later paper (Medway, *Am. Journ. Sci.*, 1904, [4], xviii., 56), its fitness for the estimation of cadmium as well as several other metals has been shown. The object of the present investigation has been to more thoroughly study the conditions under which cadmium may be estimated by this means. The apparatus used was that described in the previous papers. Since it had already been shown (*loc. cit.*) that cadmium taken in the form of the sulphate can be estimated by deposition of a solution slightly acidulated with sulphuric acid, this formed the natural point of departure.

1. In Solutions containing Sulphuric Acid.

A solution of cadmium sulphate was prepared, containing approximately 16.6 grms. of the salt to the litre of water. Portions of this solution were carefully measured from a burette, diluted to the desired volume, a few drops of dilute sulphuric acid (1:4) added, the proper connections made, and the electrolysis conducted as previously described. The results obtained upon two different solutions are given in Table I.

TABLE I.

No. of expt.	Sol. taken. C.c.	H ₂ SO ₄ Drops.	Time. Mins.	Current reading = Amperes.	N.D. ₁₀₀ . Amperes.	E.M.F. approx. Volts.	Cd found. Grm.
Solution A.							
1.	15	5	18	0.4—1.0	1.2—3.0	8	0.1111
2.	15	5	10	0.4—0.5	1.2—1.5	8	0.1090
3.	15	5	16	0.4—0.9	1.2—2.7	8	0.1115
4.	15	7	35	0.5—1.0	1.5—3.0	8	0.1117
5.	15	12	25	1.0—1.5	3.0—4.5	8	0.1115
6.	15	10	35	1.0—1.5	3.0—4.5	8	0.1120
7.	15	18	30	1.5—2.0	4.5—6.0	8	0.1119
8.	15	15	25	1.5—2.0	4.5—6.0	8	0.1117
9.	30	(a)	15	3.0—4.0	9.0—12.0	8	0.2235
10.	20	12	35	2.0—3.0	6.0—9.0	8	0.1491
11.	15	(a)	60	2.0	6.0	8	0.1120
Solution B.							
1.	20		27	1.0—1.5	3.0—4.5	7.9	0.0816
2.	25		30	2.0—3.0	6.0—9.0	7.9	0.1018
3.	25		55	2.5—4.0	7.5—12.0	7.6	0.1019
4.	30		25	2.0—2.5	6.0—7.5	12.0	0.1224
5.	30		20	1.0	3.0	7.8	0.1223
6.	30		10	1.5—2.5	4.5—7.5	7.8	0.1226
(a) Indefinite.							

In experiments numbered 1 to 4, the liquid at the end of the period indicated showed traces of cadmium remaining, but in the seven experiments following these the cadmium was all deposited upon the cathode in a satisfactory condition. These results were therefore taken as indicating the standard of the solution used, the mean of the series showing the presence of 0.007454 grm. of cadmium in each c.c. of the solution.

In a second solution which it became necessary to standardise the results given under Solution B were obtained.

The mean of these six experiments gives a value of 0.10194 grm. of cadmium for every 25 c.c. of the solution, or 0.0040776 grm. for each c.c. This value was taken as the standard whenever this solution was used.

One point which was not mentioned in the former paper (*loc. cit.*) on the estimation of cadmium by this method,

but which is of much importance, is that of dilution. The earlier experiments in this work were performed at a dilution of from 65 c.c. to 75 c.c. Much trouble was experienced, however, at this dilution; for the last traces of the metal were driven from the solution only with extreme difficulty and with much loss of time, as may be noted by comparing the time interval of most of the experiments with the shorter interval of the last two experiments of the second series, where the dilution was 45 to 50 c.c. Moreover, it was found advisable, in order to avoid mechanical loss, to deposit not more than 0.2 grm. to 0.25 grm. of the metal upon the cathode, while even smaller quantities are to be preferred. The current density must also be kept within the limits indicated; for otherwise a spongy deposit may result. Cadmium seems to be especially liable to the formation of these spongy, unweighable deposits, and the greatest difficulties experienced in this investigation have come from this behaviour of the metal.

The best condition, therefore, may be briefly summarised as follows:—Cadmium sulphate, equivalent to not more than 0.2 c.c. to 0.25 grm. of the metal, is dissolved in 45 c.c. to 50 c.c. of water; ten to fifteen drops of dilute sulphuric acid are added; and the proper connections made and the solution subjected to electrolysis as described, fifteen minutes being sufficient time for the complete deposition of the metal upon the cathode. It is not necessary to heat the liquid, as the passage of such large currents soon heats it sufficiently. When electrolysis is complete, the excess of sulphuric acid may be destroyed with a slight excess of ammonia water, the current broken, and the cathode removed, thoroughly rinsed with water and alcohol, and dried by waving over a free flame. If the deposit is not spongy the drying is a matter of only a few moments, and there is no danger of oxidising the metallic deposit. If it is preferred, the current may be reduced by interposed resistance, the rotation stopped, and the liquid readily syphoned without danger of injuring the metallic coating.

II. In Solutions containing Acetates.

The next method to be studied in its application to the rotating cathode was the use of solutions containing acetates, as recommended by Edgar F. Smith. Originally, Smith used a solution obtained by dissolving cadmium oxide in acetic acid (*Ber.*, 1878, xi., 2048), but later found that the electrolysis proceeded equally well in solutions containing the nitrate, chloride, or sulphate of cadmium with an excess of sodium acetate (*Am. Chem. Journ.*, 1880, ii., 41). In the study of the application of this method to the estimation of cadmium, taken as the sulphate, upon the rotating cathode, two methods of proceeding were followed, both of which had been previously used by Exner in his work upon the rotating anode (*Journ. Am. Chem. Soc.*, 1903, xxv., 896). In Series A, Table II., measured amounts of cadmium sulphate solution were run off from a burette, the indicated amount of sodium acetate was added in solution, a small amount of potassium sulphate was added to increase the conductivity of the solution, the whole diluted to the desired volume, and electrolysis conducted as with the solution containing sulphuric acid. In Series B, the cadmium in the measured solution was precipitated as the hydroxide with a sodium hydrate solution, the precipitate dissolved in a very slight excess of acetic acid, potassium sulphate added as before, and the solution subjected to electrolysis.

In both series the volume of the solution was about 60 c.c. to 65 c.c. The sixth experiment in each series will indicate the result when the greater concentration of 45 c.c. to 50 c.c. was tried. In these cases the precipitate showed a tendency to sponginess, which was more noticeable in Series A. At the greater dilution, the deposition of the cadmium proceeds rapidly and satisfactorily; the deposit is rather crystalline, fairly compact, and easily washed, so that the method forms one of the very best where the cadmium is taken in the form of the sulphate; the chloride and nitrate behave differently, and will be treated later. The second modification seemed to give deposits more

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, xx., p. 268.

TABLE II.

No.	Cd taken. Grm.	NaOC ₂ H ₃ O. Grms.	K ₂ SO ₄ . Grm.	Current reading = Ampères.	N.D.100. Ampères.	E.M.F. Volts.	Time. Minutes.	Cd found. Grm.	Error. Grm.
Series A.									
1.	0.1864	1.5	0.5	2.0	6.0	8.0		(a)	—
2.	0.1491	2.0	1.0	1.5	4.5	8.0	15	(b)	—
3.	0.1118	0.5	1.0	1.0	3.0	8.0	20	0.1121	+0.0003
4.	0.1491	1.5	0.5	0.9	2.7	8.0	15	0.1494	+0.0003
5.	0.1491	1.5	0.5	0.9	2.7	8.0	15	0.1496	+0.0005
6.	0.1223	1.5	0.5	0.75	2.25	7.5	20	0.1237	+0.0014
Series B.									
1.	0.1491	NaOH. Excess	0.5	1.25	3.75	8.0	10	0.1496	+0.0005
2.	0.1491	0.2	0.5	0.8	2.4	8.0	15	0.1491	0.0000
3.	0.1491	0.2	0.5	0.8	2.4	8.0	15	0.1493	+0.0002
4.	0.1223	0.5	0.2	1.0	3.0	12.0	20	0.1223	0.0000
5.	0.1223	0.5	0.2	1.0	3.0	12.0	20	0.1223	0.0000
6.	0.1223	0.2	0.5	1.25	3.75	7.5	10	0.1227	+0.0004

(a) Did not weigh, as precipitate was non-adherent. Current too high for quantity of cadmium present.

(b) Deposits spongy and blistered. Too much electrolyte present.

TABLE III.

No.	Cd taken. Grm.	NaOH. Grms.	KCN. Grm.	Current reading = Ampères.	N.D.100. Ampères.	E.M.F. Volts.	Time. Minutes.	Cd found. Gem.	Error. Grm.
1.	0.1491	1.5	0.5	2.5	7.5	8	35	0.1498	+0.0007
2.	0.1491	1.0	0.5	2.5—4.5	7.5—13.5	8	30	0.1490	-0.0001
3.	0.1223	1.5	1.0	2.5	7.5	8	35	0.1225	+0.0002

TABLE IV.

No.	Cd taken. Grm.	Na ₂ P ₂ O ₇ . Grm.	NH ₄ OH.	Current = Ampères.	N.D.100. Ampères.	E.M.F. Volts.	Time. Minutes.	Cd found. Grm.	Error. Grm.
Series A.									
1.	0.1491	0.5	15 c.c. (1 : 4)	1.0—1.5	3.0—4.5	8	15	0.1498	+0.0007
2.	0.1491	0.5	Excess	0.4	1.2	8	15	0.1489	-0.0002
3.	0.1864	0.5	15 c.c. (conc.)	0.7	2.1	8	15	0.1869	+0.0005
Series B.									
4.	0.1491	1.0	H ₃ PO ₄ (17 sp. gr.). 1.0 c.c.	1.0	3.0	8	30	0.1496	+0.0005
5.	0.1864	1.0	1.0 "	1.0—1.5	3.0—4.5	8	30	0.1857	-0.0006
6.	0.1491	1.0	1.0 "	1.0	3.0	8	30	0.1493	+0.0002
Series C.									
7.	0.1491	1.0	H ₂ SO ₄ . 2 c.c. (1 : 4)	2.0—2.5	2.0—7.5	8	30	0.1501	+0.0010
8.	0.1864	0.5	Excess	1.0—2.0	3.0—6.0	8	35	0.1862	-0.0002
Series D.									
9.	0.1491	0.5	HCl. Slight excess	1.0	3.0	8	37	0.1499	+0.0008
10.	0.1491	0.5	" "	1.0	3.0	8	36	0.1486	-0.0005

In Nos. 1 and 3 a small amount of dilute sulphuric acid was added to increase the conductivity of the solution, but the time was not reduced thereby, while the resulting deposit was slightly spongy.

In No. 5 the calcium was not quite all precipitated. In No. 7 the precipitate was spongy.

TABLE V.

No.	Cd taken. Grm.	HNa ₂ PO ₄ . Grm.	H ₂ PO ₄ (1:7). C.c.	Total vol C.c.	Current = Ampères.	N.D.100. Ampères.	E.M.F. Volts.	Time. Minutes.	Cd found. Grm.	Error. Grm.
1.	0.1491	0.5	1.0	75	1.0—1.2	3.0—3.6	8	20	0.1477	-0.0014
2.	0.1491	0.5	5.0	75	2.0—2.5	6.0—7.5	8	23	0.1496	+0.0005
3.	0.1491	0.5	5.0	75	2.0—1.5	6.0—4.5	8	30	0.1508	+0.0017
4.	0.1491	0.5	3.0	75	2.5	7.5	12	25	0.1502	+0.0011
5.	0.1491	0.5	4.0	75	2.5	7.5	8	25	0.1485	-0.0006
6.	0.1491	0.5	2.0	75	2.5	7.5	12	35	0.1501	+0.0010
7.	0.1864	0.25	2.0	75	2.0—3.0	6.0—9.0	12	40	0.1861	-0.0003
8.	0.1491	0.3	1.5	75	3.5	10.5	12	30	0.1502	+0.0011
9.	0.1019	0.25	5.0	75	2.5—3.0	7.5—9.0	7.8	30	0.1024	+0.0005
10.	0.1019	0.25	5.0	75	3.0—3.5	9.0—10.5	7.8	30	0.1027	+0.0008
11.	0.1223	0.2	5.0	75	3.0—3.5	9.0—10.5	7.8	40	0.1221	-0.0002

No. 1.—Not all out.

No. 2.—Slight yellow colour with H₂S.

No. 3.—Slight yellow with H₂S.

No. 4.—Spongy.

No. 5.—Not all out.

No. 6.—Spongy.

No. 10.—Spongy.

No. 11.—Slight test with H₂S.

satisfactory than the first. Certain cautions, however, are to be observed. Not more than 0.1500 grm. may safely be estimated; the normal current density should not exceed 3.0 amperes if a spongy deposit is to be avoided; and, for the same reason, a large excess of electrolytes is to be avoided.

III. In Solutions containing Cyanides.

The deposition of cadmium from a solution of the double cyanide has always been very satisfactory, and the results with the rotating cathode were in complete accordance with previous work on this method. The range of conditions of current and quantity of electrolyte is broad, the deposit is a beautiful silvery plate, so compact as to be rubbed off only with difficulty, which dries very quickly; and although the complete deposition of the metal is not so rapid as it is from solutions containing sulphates or acetates, it is sufficiently rapid. Care should be taken to avoid foaming of the solution, as this retards somewhat the deposition of the final traces of cadmium. Generally, a volume of 65 c.c. to 70 c.c. was found most satisfactory. The solution was run off into a beaker of convenient size, the cadmium precipitated with sodium hydroxide, and the precipitate re-dissolved in potassium cyanide. The results obtained are given in Table III.

IV. In Solutions containing Pyrophosphates.

Brand (*Zeit. Anal. Chem.*, 1889, xxviii., 581) has recommended the use of a solution containing sodium pyrophosphate for the electrolytic estimation of metals, among others, cadmium; and the fitness of this solution for use with the rotating cathode was now studied. In each case the cadmium was precipitated with the indicated amount of sodium pyrophosphate, the precipitate dissolved in an excess of ammonium hydroxide (Series A), phosphoric acid of 1.7 specific gravity (Series B), sulphuric acid (Series C), or hydrochloric acid (Series D), and subjected to the action of the current. The volume of the solution was 60 c.c.

While fairly accurate results may be obtained, the method is neither so accurate as those previously described, nor are the conditions so flexible. Particular care must be used to avoid too large a current, as a spongy deposit may result. Table IV. gives the results obtained.

V. In Solutions containing Phosphates.

The use of a solution containing the orthophosphates dissolved in phosphoric acid has been recommended by Smith (*Am. Chem. Journ.*, 1890, xii., 329), and this solution was next tried. The results given in Table V. will show the scope of the modifications tried.

From this series of experiments it may be seen that the method may be made to give fair results if the following conditions are closely adhered to:—For a total volume of 75 c.c., the cadmium is precipitated with 0.25 grm. of hydrogen disodic phosphate, 5 c.c. of phosphoric acid (sp. gr. = 1.7 added), and the solution electrolysed with a current of about 8 volts potential. If the normal current density does not exceed 9 amperes, the deposit will be fair, and complete in about thirty minutes.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., His Grace the Duke of Northumberland, K.G., F.R.S., President, in the Chair. Mr. Cyril Davenport, Mr. G. S. Hein, Sir Henry Kimber, Bart., M.P., Major P. A. MacMahon, and Mrs. Roberts were elected Members. Prof. A. Righi, Prof. P. Lenard, Prof. W. C. Röntgen, Prof. J. H. van't Hoff, Prof. T. W. Richards, Prof. A. von Bayer, Prof. K. J. Ångström, and Prof. H. H. Hildebrandsson were elected Honorary Members of the Royal Institution. The Special Thanks of the Members were returned to Dr. M. M. Bleekrode for his gift of a portrait of the late Dr. L. Bleekrode, Hon. Mem. R.I.

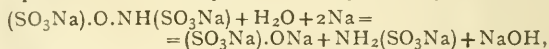
HYDROXYLAMINE- $\alpha\beta$ -DISULPHONATES.*

STRUCTURAL ISOMERIDES OF HYDROXIMINO-SULPHATES OR HYDROXYLAMINE- $\beta\beta$ -DISULPHONATES.

By TAMEASA HAGA,
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In a previous paper (*Journ. Coll. of Sci., Imp. Univ., Japan*, xix., Art. 15), it was shown that Fremy's *meta*-sulphazilate, which till then had been considered to be constituted as an amine oxide, $O : N(SO_3K)_3$, is in reality a *hydroxylaminetrisulphonate*. The nature of the products of the proximate hydrolysis of the metasulphazilates seems to afford the strongest additional evidence that these salts are hydroxylaminesulphonates and, as such, mixed anhydrides of an acid sulphate and a hydroxylaminedisulphonate.

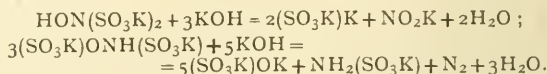
The ultimate hydrolysis of a hydroxylaminetrisulphonate, through intermediate stages, into hydroxylamine and an acid sulphate, is difficult to carry to completion (*Journ. Coll. of Sci., Japan*, xix., Art. 15, 28), but the first stage of it, into a hydroxylaminedisulphonate and one-third of the quantity of acid sulphate that is produced in the ultimate hydrolysis, is very easily accomplished. The hydroxylaminedisulphonate thus obtained proves to be an entirely new salt, structurally isomeric with the corresponding *hydroxylaminedisulphonate* (Fremy's *sulphazotate*), from which it differs greatly in essential physical and chemical properties. The one is a $\beta\beta$ -derivative, the other an $\alpha\beta$ -derivative of hydroxylamine. Which is which is determined by the behaviour of the two salts towards sodium amalgam. A salt of the series already known remains unaffected, whilst one of the new series decomposes (see *prox.*) into sulphate and aminemonosulphonate (sulphamate, aminosulphate), just as its parent salt, hydroxylaminetrisulphonate decomposes, in like circumstances, into sulphate and aminedisulphonate (iminosulphate). It must, therefore, have the $\alpha\beta$ -constitution, as shown in the following equation, framed to express its decomposition by sodium:—



and the other salt have the $\beta\beta$ -constitution which it has always been assumed to have, $HON(SO_3Na)_2$. The activity of the $\alpha\beta$ -salts towards sodium amalgam serves also to demonstrate their sulphatic constitution (derived from that of the hydroxylaminetrisulphonates) as the mixed anhydrides of an acid sulphate and a hydroxylamine-mosulphonate.

(Two other examples of such mixed sulphatic anhydrides are any hydroxylaminetrisulphonate and any hyponitrososulphate. Raschig, *Zeit. Angew. Chem.*, 1905, xviii., 1309, has recently adduced evidence that nitrosyl sulphate is, after all, not a sulphate but a nitrosulphonate, $O_2N.SO_3H$).

The action of potassium hydroxide upon the two salts seems clearly to establish the difference there is in their constitution. The old salt reverts to nitrite and sulphite when it is left, even in the cold, in a concentrated solution of the alkali (*Journ. Coll. of Sci., Japan*, vii., 40), whereas the new salt is only incompletely decomposed into sulphate, aminemonosulphonate, and nitrogen (see *prox.*), after several hours' digestion at 100° to 125° with the alkali. These results are exhibited by the following equations, the upper for the old or $\beta\beta$ -salt, and the lower for the new or $\alpha\beta$ -salt:—

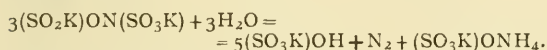


The lower of these equations recalls the action of heated alkalis upon hydroxylamine (Lossen) and upon hydroxylaminemonosulphonate (Claus). The upper equation brings out strongly the oximide constitution of the $\beta\beta$ -salt.

It is an interesting fact that the course of the hydrolysis

* *Journal of the College of Science, Imperial University, Tokyo, Japan*, xxi., Article 6.

of the two salts in acidified solution is widely different, but it is a fact which cannot apparently be used to establish the nature of the difference in their constitution. The $\beta\beta$ -or long-known salt, by losing one of its two sulphonate groups, readily passes into the hydroxylamine- β -monosulphonate, $\text{HONH}(\text{SO}_3\text{K})$, whereas the new or $\alpha\beta$ -disulphonate (see *prox.*) passes much less easily into acid sulphate and hydroxylamine itself (and products of its well-known decomposition), without ever affording evidence of any production of a monosulphonate, which in this case should have the α -constitution, expressed by $(\text{SO}_3\text{K})\text{ONH}_2$, and, as an amidogenium salt, be perhaps incapable of existence. The slowness with which an $\alpha\beta$ -salt begins to hydrolyse is illustrated by the fact that a solution of the potassium salt will remain clear for five minutes at the common temperature after it has been mixed with hydrochloric acid and barium chloride, whereas a solution of the $\beta\beta$ -salt will almost at once begin to show turbidity. When the hydrolysis of the $\alpha\beta$ -salt proceeds in the absence of much or any hydrochloric acid, nitrogen and ammonia very largely take the place of the hydroxylamine which is obtained in nearly the theoretical quantity when the salt hydrolyses in presence of a sufficiently concentrated hydrochloric acid solution. The following equation expresses what principally happens in the absence of hydrochloric acid:—



Silver oxide and lead peroxide seem to be without action upon the $\alpha\beta$ -salts in solution; they certainly do not produce the deeply coloured peroxylaminesulphonate which so strikingly results from their action upon the $\beta\beta$ -salts. This difference accords with that indicated in the constitution of the two series of salts. A hydroxylamine- $\alpha\beta$ -disulphonate also unexpectedly agrees with a hydroxylamine- $\beta\beta$ -disulphonate in not reducing copper or silver oxide in alkaline solution and is also inactive upon a solution of iodine in presence of sodium acid carbonate. A hydroxylaminemonosulphonate, $\text{HONH}(\text{SO}_3\text{K})$, which, like it, has an aminic hydrogen atom in its constitution, has the activity of hydroxylamine upon both alkaline copper solution and upon alkali-bicarbonate iodine solution.

Like the $\beta\beta$ -salts the hydroxylamine- $\alpha\beta$ -disulphonates decompose with gentle explosion when heated. Also, like the $\beta\beta$ -series, that of the $\alpha\beta$ -disulphonates includes highly alkaline normal salts, such as $(\text{SO}_3\text{K})\text{ONK}(\text{SO}_3\text{K})$ and $(\text{SO}_3\text{Na})\text{ONNa}(\text{SO}_3\text{Na})$.

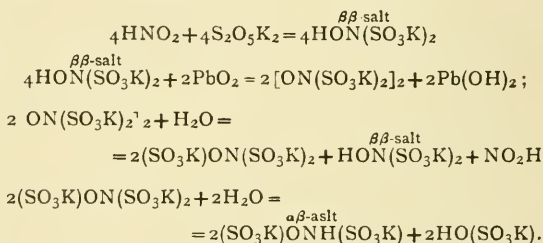
A concentrated solution of the disodium salt is not precipitated by silver nitrate, mercuric nitrate, lead nitrate, or barium chloride. A concentrated solution of basic lead acetate precipitates from it an oil, which becomes crystalline on standing. A concentrated solution of a potassium salt precipitates from it the very much less soluble potassium salt. Barium hydroxide gives a voluminous, apparently amorphous, precipitate, probably of a sodium barium salt.

The molecular magnitude of the normal or trisodium hydroxylamine- $\alpha\beta$ -disulphonate (see *prox.*), as determined cryoscopically by means of melted Glauber's salt (Löwenherz), is that expressed by $\text{O}_7\text{N}_2\text{S}_2\text{Na}_3$, the same, therefore, as that found for the normal sodium $\beta\beta$ -salt (*Journ. Coll. of Sci., Japan*, xix., Art. 15, 33). Remarkably, however (and it is a unique experience with this method, so far as has been ascertainable), the depression of the solidifying point of the sodium sulphate is at first much less than that which corresponds with the simple molecular weight, the number for which it only reaches and remains steady at, in the course of an hour or two and after several repetitions of re-melting and solidifying. It would seem from this that the solid salt consists of associated simple molecules which require time to separate from each other after dissolution in melted Glauber's salt.

The discovery of this new series of salts, establishing as it does the existence of significant structural isomerism in other than carbon compounds, should prove to be of very special interest, there being hardly any other instance

known, except that of nitramine with hyponitrous acid, the existence of which is disputed by Hantzsch (*Zeit. Anorg. Chem.*, 1898, xix., 106), just because it would be the only case known in inorganic chemistry.

The subjoined scheme of equations may serve to show at a glance the relation by derivation of the new series of salts to the old series. A hydroxylamine- $\beta\beta$ -disulphonate, a salt formed by the union of nitrous acid with a metasilphite, is oxidisable wholly into a peroxylamine-sulphonate. This, by hydrolysis in presence of an alkali, becomes, to the extent of half its nitrogen, hydroxylaminetrisulphonate; to the extent of a fourth of its nitrogen, the $\beta\beta$ -salt again; and, to the extent of the remaining fourth of its nitrogen, nitrous acid (nitrite) again. Lastly, by acid hydrolysis, the hydroxylaminetrisulphonate becomes sulphate and a hydroxylamine- $\alpha\beta$ -disulphonate. From this it will be seen that, at most, only the half of the $\beta\beta$ -salt comes out as the $\alpha\beta$ -salt, one-fourth of it being regenerated and the remaining fourth reverting to its parent salts, of which the sulphite has suffered oxidation to sulphate.



The return of an $\alpha\beta$ -salt to the state of its $\beta\beta$ -isomeride can hardly be looked upon as possible, its own production having been due to oxidation of a fourth of the sulphonate groups into acid sulphate.

Salts.

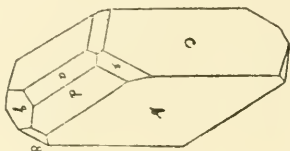
Dipotassium Hydroxylamine- $\alpha\beta$ -disulphonate, $(\text{SO}_3\text{K})\text{ONH}(\text{SO}_3\text{K})$.—Potassium hydroxylaminetrisulphonate, dissolved in ten times its weight of warm water (it is much less soluble in cold water—*Journ. Coll. of Sci., Japan*, xix., Art. 15, 8), soon begins to hydrolyse when its solution is quickly cooled and mixed with a drop of dilute sulphuric acid just before it would otherwise crystallise out again. The hydrolysis, to the end of its first stage, is complete in about four days. When the solution is deprived of sulphate and neutralised by the addition of barium carbonate or hydroxide, filtered, and evaporated, the new disulphonate is obtained in crystals, to the extent of at least two-thirds of the calculated yield. That hydrolysis of the trisulphonate proceeds to the extent shown in the equation (see *prox.*) in about four days and then proceeds much more slowly, has been ascertained both acidimetrically and by estimation of the sulphuric acid produced.

The dipotassium salt is an anhydrous salt, about twice as soluble in water as the corresponding (but hydrated) $\beta\beta$ -salt. Of it 6.44 parts at 16.4°, 7.18 parts at 17.8°, and 8.05 parts at 20° dissolve in 100 parts of water. Its solution is neutral to litmus, to methyl-orange, and to phenolphthalein.

The salt forms hard monoclinic prisms which are sometimes short thick prisms, sometimes flattened tables, and sometimes long slender prisms or needles. Crystals of the one or other habit generally re-crystallise in that habit, but the salt is not dimorphous. A saturated solution of one form of the salt is saturated also towards another form of it, whilst the two forms will lie side by side unchanged for a length of time in the same mother-liquor. Prof. Jimbo has kindly supplied the following account of his examination of a short thick prism:—A monoclinic crystal, developed perfectly on one end of the clinodiagonal, about 6 m.m. long, was measured by means of a contact goniometer, only two angles, ce and ed , having been

measured by reflection. The faces *a* and *g* were depressed; the other faces also did not give good images. Seven faces were recognised; one other could not be determined.

(a)	$\infty P\infty$	<i>bd</i> = $133^{\circ} 25'$
(b)	$\infty P\infty$	<i>ce</i> = $144^{\circ} 27'$
(c)	∞P	<i>ef</i> = $127^{\circ} 53'$
(d)	∞P	<i>ed</i> = $141^{\circ} 25'$
(e)	$-P$	<i>df</i> = $126^{\circ} 15'$
(f)	$P(?)$	<i>cg</i> = 117°
(g)	$\frac{1}{2}P\infty(?)$	



The results of analyses, of (A) the tabular form and of (B) the acicular form of the salt, are as follows:—

A.	0.2863 gave 0.1845 potassium sulphate.	Potassium = 28.98
	0.2105 gave 0.3673 barium sulphate.	Sulphur = 23.96
	0.2739 gave 12.58 c.c. moist nitrogen at 19.5° and 756.1 m.m.	Nitrogen = 5.22
B.	0.2679 gave 0.1751 potassium sulphate.	Potassium = 28.74
	0.2684 gave 11.9 c.c. moist nitrogen at 16.7° and 765.5 m.m.	Nitrogen = 5.19

$\text{HO}_7\text{NS}_2\text{K}_2$ requires potassium, 29.06; sulphur, 23.79; nitrogen, 5.21 per cent. In all analyses given in this paper sulphur was determined by heating the salt with hydrochloric acid in a sealed tube at 180° for five hours or at 200° for two hours.

Tripotassium Hydroxylamine- $\alpha\beta$ -disulphonate, $(\text{SO}_3\text{K})\text{ONK}(\text{SO}_3\text{K})_2 \cdot 2\text{H}_2\text{O}$.—This salt is precipitated, at first as an oil, when alcohol is added to its concentrated aqueous solution, prepared by dissolving the disulphonate in a little hot water and adding to it the calculated quantity of potassium-hydroxide solution. The oily salt slowly solidifies into lumps of microscopic crystalline plates. The quantity obtained should be about equal in weight to that of the disulphonate used, the calculated quantity being five parts from four. It is very soluble in water. Its solution is not precipitated by barium chloride, in this respect being unlike a solution of the corresponding $\beta\beta$ -salt. It is caustic in taste, and explodes suddenly when heated.

Analysis.

0.1696 gave 0.1286 potassium sulphate.	Potassium = 34.05
0.2588 gave 0.1944 potassium sulphate.	Potassium = 33.73
0.1568 gave 0.2343 barium sulphate.	Sulphur = 20.52
$\text{H}_4\text{O}_9\text{NS}_2\text{K}_3$ requires potassium, 34.18; sulphur, 18.66 per cent.	

The **disodium salt**, $(\text{SO}_3\text{Na})\text{ONH}(\text{SO}_3\text{Na})$, is like the $\beta\beta$ -salt, anhydrous. The very soluble sodium hydroxylamine-trisulphonate is dissolved in five times its weight of water and acidified with dilute sulphuric acid. In two or three days, at the ordinary temperature, it will have all hydrolysed, and the solution is then to be neutralised with sodium carbonate. On exposure for a night in the ice chamber, almost all the sodium sulphate will crystallise out, and then the mother-liquor can be evaporated to get the new salt. Like corresponding $\beta\beta$ -salt, this salt forms hard masses firmly adhering to the sides of the vessel. These masses are stellar or warty groups of microscopic

thick rhombic plates. The salt is exceedingly soluble in water, from which it can be nearly all precipitated by alcohol. Two preparations of the salt were analysed (I. and II.):—

I.	0.2209 gave 0.1313 sodium sulphate.	Sodium = 19.28
	0.1059 gave 0.2096 barium sulphate.	Sulphur = 27.17
	0.5151 gave 26.45 c.c. moist nitrogen at 17° and 756.8 m.m.	Nitrogen = 5.94
II.	0.2509 gave 0.1502 sodium sulphate.	Sodium = 19.41
	0.0959 gave 0.1910 barium sulphate.	Sulphur = 27.35

$\text{HO}_7\text{NS}_2\text{Na}_2$ requires sodium, 19.43; sulphur, 27.02; nitrogen, 5.92 per cent.

The **trisodium salt**, $(\text{SO}_3\text{Na})\text{ONNa}(\text{SO}_3\text{Na})_2 \cdot 2\text{H}_2\text{O}$, is prepared just in the same way as the tripotassium salt. It is obtained as a crystalline powder. For determinations of its molecular magnitude, see *prox.*

0.1450 gave 0.1054 sodium sulphate.	Sodium = 23.57
0.2269 require 7.56 c.c. N/10 hydrochloric acid with methyl-orange as indicator.	Alkalinity as sodium = 7.66
0.3594 gave 0.5698 barium sulphate.	Sulphur = 21.75
$\text{H}_4\text{O}_9\text{NS}_2\text{Na}_3$ requires sodium 23.41; alkalinity sodium, 7.8; sulphur, 21.71 per cent.	

Diammonium salt, $(\text{SO}_3\text{NH})\text{ONH}(\text{SO}_3\text{NH}_4)$.—Ammonium hydroxylaminetrisulphonate (*Journ. Coll. of Sci., Japan*, xix., Art. 15, 9) hydrolyses in the same way as the sodium salt. The ammonium acid-sulphate is got rid of by adding just enough barium hydroxide solution, filtering, and evaporating, at first at a gentle heat, and then in the cold over sulphuric acid under reduced pressure. It occurs as small thick plates, which are somewhat hard, and as nodules composed of minute tabular crystals. It is a very soluble salt, 3 parts dissolving normally in just 2 parts of water at 18° , but it is very apt to form supersaturated solutions. It is a more stable salt than the corresponding $\beta\beta$ -salt. Its crystals are probably anhydrous, but those analysed showed the presence of 0.25 H_2O per molecule.

0.3559 gave 0.7189 barium sulphate.	Sulphur = 27.74
0.2320 gave 35.5 c.c. moist nitrogen at 16.2° and 754.5 m.m.	Nitrogen (per cent) = 18.18
$\text{H}_9\text{O}_7\text{N}_3\text{S}_2$ requires sulphur, 28.21; nitrogen, 18.53.	
With $\frac{1}{2}\text{H}_2\text{O}$ added, it requires sulphur, 27.66; nitrogen, 18.17 per cent.	

Barium Salts.—Barium salts have not been prepared in a state suited for satisfactory determination of their nature. Evaporation of a solution of the ammonium salt with excess of barium hydroxide in a vacuum over sulphuric acid to a small volume removed all ammonia. After removal of the excess of barium hydroxide by carbon dioxide, the filtered solution was further evaporated in the desiccator. First, a viscid liquid and then a bulky friable, porous mass, devoid of crystalline character, were obtained. The latter was not quantitatively analysed, but it yielded, when hydrolysed, barium sulphate and hydroxylamine sulphate in crystals which were further identified by a very satisfactory sulphuric acid determination. The product was therefore undoubtedly a barium hydroxylamine- $\alpha\beta$ -disulphonate. By using less barium hydroxide, crystallised ammonium barium salts of varying composition may be obtained. One quantitatively examined had a composition corresponding fairly well with that of a compound of six molecules of the diammonium salt with one molecule of the two-thirds normal barium salt.

Molecular Magnitude of Trisodium Hydroxylamine- $\alpha\beta$ -Disulphonate.

By Löwenherz's method, the molecular magnitude of the trisodium hydroxylamine- $\beta\beta$ -disulphonate has been found to be (anhydrous) 233 and 239.6, whilst $\text{O}_7\text{NS}_2\text{Na}_3$ requires 259.35 (*Journ. Coll. Sci., Japan*, xix., Art. 15, 33). By the same method, the following approximations to the

same number have been obtained for the $\alpha\beta$ -salt, namely, 269.6, 279.3, and 256.4, using the constant, 32.6, for sodium sulphate found by Löwenherz. The details of these determinations of the molecular magnitude of the $\alpha\beta$ -salt are specially interesting (see above). Of this salt, 0.8371, dissolved in 40.48 melted Glauber's salt, produced a depression of 0.22° in the crystallising point, corresponding with the molecular weight, 306.2. After solidifying and melting three times, the depression reached 0.24° , and remained at that, which corresponds with 269.6. There was now added 0.5848 more of the salt, and the depression due to this addition was at first only 0.005°, corresponding with a molecular weight of 9416; that is about forty times the normal magnitude. On allowing the mixture to solidify and re-melt, the depression grew in amount until at the sixth repetition it reached its maximum, corresponding with the simplest formula of the salt. The whole quantity, 1.4219, now caused a depression which gave the molecular magnitude as 279.3. Adding now 0.9026, the additional depression was at first only 0.04°, corresponding with a molecular weight of 1878, which is about eight times the simple molecule. But, again, as before, after several times repeated melting and solidifying, the normal depression was reached and remained constant, and the total quantity of the salt, namely, 2.3245, gave a depression of 0.73° , indicating the molecular magnitude, 256.4.

Reduction of the Disodium Salt by Sodium Amalgam.

Disodium hydroxylamine- $\alpha\beta$ -disulphonate, 0.4811 grm., was shaken with 12 grms. of 3 per cent sodium amalgam (which acts very slowly on it) and left with it, with occasional shaking, for three days. Much sodium remained unconsumed. The solution was rendered neutral to phenolphthalein by acetic acid, and the sulphate present precipitated as barium sulphate. Of the sulphur in the quantity of salt taken, 13.73 per cent were thus found as sulphate, instead of 13.51, the calculated third. The aminemonosulphonate in the filtrate from this sulphate was hydrolysed by heating the solution at 150° for three hours in a sealed tube with hydrochloric acid. It thus yielded the rest of the sulphur as sulphate, a result which, effected at such a temperature, showed that that sulphur was all in direct union with nitrogen and that none of the hydroxylaminedisulphonate had been left undecomposed by the sodium. As a check, the ammonia, the other product of the hydrolysis of the aminemonosulphonate, was also determined and found equal to 5.5 per cent instead of 5.94 per cent, the full amount. The production of aminemonosulphonate by the reduction of the hydroxylamine- $\alpha\beta$ -disulphonate was further established quantitatively in a separate experiment, in which, after the reduction, the aminesulphonate was precipitated characteristically by mercuric nitrate and the acid itself, after recovery from its mercury salt, crystallised out, and otherwise tested.

(To be continued).

impossible provided the directions are followed. The choice of substances to be prepared is excellent; some which are comparatively rare, but whose preparation has specially interesting features, being included; thus, for example, the nature of colloidal solutions and their preparation are discussed. All the methods described have been thoroughly tested, and the book can be confidently recommended to be used as a guide for laboratory work to supplement a course of qualitative analysis.

Smaller Chemical Analysis. By G. S. NEWTH, F.I.C., F.C.S. London, New York, and Bombay: Longmans, Green, and Co. 1906.

THIS book is an abridged edition of the qualitative section of the author's manual of qualitative and quantitative chemical analysis, which is already well known as a valuable work. The book contains an ordinary analytical course for the detection and separation of bases and radicals, grouped in the usual way, and gives general tables of dry and wet reactions with full directions and copious explanations. In addition a section is given on simple volumetric determinations, typical examples being included of neutralisation, oxidation, reduction, and precipitation processes, so that the book is very suitable for the use of candidates for the Senior Locals and similar examinations.

Ausführliches Lehrbuch der Pharmazeutischen Chemie. ("Complete Text-book of Pharmaceutical Chemistry"). Volume I., Part I. By Dr. ERNST SCHMIDT. Fifth Edition. Braunschweig: Friedrich Vieweg und Sohn. 1906.

THE first volume of the fifth edition of this treatise deals with inorganic chemistry, and discusses the general physical and chemical properties and relations of the most important inorganic substances, their uses in medicine being specially emphasised. A thoroughly good grounding in inorganic chemistry is of great importance to pharmaceutical chemists, and with the help of this book the student should be enabled to lay a firm foundation for later and more advanced work, for the author has been careful to include descriptions of all those substances which are in any way connected with pharmaceutical chemistry, so that a more extended course is given than is generally considered necessary. Methods of detection and quantitative determination of the more important elements and compounds are described, and an introduction gives a short account of the theory of chemistry.

Die Elektrochemischen Deutschen Reichspatente. ("German Electro-chemical Patents"). By Dr. P. FERCHLAND and Dr. P. REHLÄNDER. Halle-a-S.: Wilhelm Knapp. 1906.

THESE extracts from the German patent specifications will be a great assistance to the chemist who, in order to solve some technical electro-chemical problem, may be called upon to undertake the lengthy task of searching the records, and who has hitherto had no guide to aid him in this search. The class, number, and title of each patent is given, with the name of the patentee, and a short, and in some cases illustrated, abstract of the most important points in the specification; by means of an appendix the patents have been brought down to the latest possible date, while a list is given of the numbers of the patents which were still in force at the end of May, 1906. The merits and value of the processes are not, as a rule, criticised except when the editors have had special reasons for so doing. The extremely tedious work of preparing such a list as this must have taxed the patience of the compilers, but it was well worth doing, and will be appreciated by many; the book is well arranged, and valuable cross references are given which will be an additional help to those who want full information regarding the patents relating to any special question.

NOTICES OF BOOKS.

Practical Methods of Inorganic Chemistry. By F. MOLLWO PERKIN, Ph.D. London: Archibald Constable and Co., Ltd. 1906.

THE training in preparative inorganic chemistry which is provided in this book should be of great value to the student, and should help to fix his knowledge of both general and special methods in inorganic chemistry, which are usually not so much emphasised as the corresponding processes in organic work. Although the larger text-books will be found to contain details of the preparation of most of the substances described in this book the arrangement of them in groups is a point which will recommend the manual, and the experimental details are so fully and carefully explained that failure should be

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements before Easter:—Mr. W. Duddell, a Christmas course of six experimentally illustrated lectures on "Signalling to a Distance—from Primitive Man to Radiotelegraphy," adapted to a juvenile auditory; Prof. Percy Gardner, two lectures on "The Sculpture of Aegina in Relation to Recent Discovery"; Prof. A. C. Seward, two lectures on "Survivals from the Past in the Plant World"; Prof. W. Stirling, six lectures on "The Visual Apparatus of Man and Animals"; Dr. W. N. Shaw, two lectures on "Recent Advances in the Exploration of the Atmosphere"; Major P. A. MacMahon, two lectures on "The Standards of Weights and Measures"; Prof. W. W. Watts, two lectures on—(1) "The Building of Britain," (2) "Recent Light on Ancient Physiographies"; Dr. W. Martin, two lectures on "Old Dutch Painting and Painters"; Dr. C. W. Saleeby, two lectures on "Biology and Progress"; Sir Alexander Mackenzie, two lectures on "Latest Phases of Music" (with musical illustrations); and Prof. J. J. Thomson, six lectures on "Röntgen, Cathode, and Positive Rays." The Friday Evening Meetings will commence on January 18, when Sir Andrew Noble will deliver a Discourse on "Fifty Years of Explosives." Succeeding Discourses will probably be given by Mr. Charles Welch, Sir Alroth E. Wright, Prof. I. Gollancz, Mr. J. J. Lister, Mr. Dugald Clerk, Prof. D. J. Hamilton, Prof. J. J. Thomson, Prof. G. Lunge, and other gentlemen.

The Tensile Strength of Copper-tin Alloys.—E. S. Shepherd and G. B. Upton (*Journ. Phys. Chem.*, ix., 441).—This paper gives an account of an extended study of the mechanical properties of copper-tin alloys between 100 and 70 per cent of copper. In planning the experiments as well as in analysing the results, the copper-tin diagram was referred to. The test pieces were chill-cast in graphite moulds, and, in general, no machining was necessary to reduce them to the proper dimensions, which were 0.42 inch diameter and 3 inches length of cylinder. Numerous precautions had to be taken to insure reliable castings, particularly in the range from 94 to 87 per cent copper. As it was, some results had to be rejected. Tests on the ultimate tensile strength and per cent of elongation were carried out for interval of composition of 2 or 3 per cent for the most part. Tests were made on specimens as follows:—(1) Directly after casting; (2) after being heated for a week at 540°, and then quenched in water; (3) after being heated for a week at 400°, and then slowly cooled; and (4) after being brought to a medium red-heat and quenched. From 100 to 87 per cent copper the heat treatment had little effect on the ultimate strength of the alloy. From 87 to 76 per cent marked differences appear. Treatment (3) gives the weakest casting, while the other treatments gave increasing strength in the order (1), (2), (4). At 81 per cent the strength for treatment (3) was found to be 43,000 pounds per square inch, while for (4) it was found to be 63,000 pounds. The general result is therefore that annealing below red-heat tends to lessen the strength. The differences found between quenching from 540° after a week's heating and from red-heat after brief heating, are probably due to a coarser crystalline structure in the former. In the neighbourhood of 80 per cent copper the maximum strength is reached, after which the strength falls off abruptly, so that at 70 per cent it lies below 20,000 pounds, and is very uncertain, being almost zero in some cases. As regards ductility (per cent elongation) those pieces tested immediately after casting exhibit a slight maximum at 98 per cent. At this composition specimens subjected to other treatment exhibit a slightly higher ductility. Beyond this composition the test pieces annealed for a week at 400° and 540° show increasing ductility which reaches a maximum at about 87 per cent, the per cent elongation reaching 39 per cent for pieces annealed at 540°. Beyond 87 per cent the ductility falls off rapidly. Stress and strain curves were obtained for a number of

compositions. Whatever the treatment, the curves rise regularly, and show no signs of a point of maximum load as do iron and steel.—*Journ. Am. Chem. Soc.*, xxviii., No. 10.

MEETINGS FOR THE WEEK.

- MONDAY, 10th.**—Society of Arts, 8. (Cantor Lectures). "Artificial Fertilisers—their Nature and Functions," by A. D. Hall.
- WEDNESDAY, 12th.**—Society of Arts, 8. "Fruit Growing and Protection of Birds," by C. H. Hooper.
- THURSDAY, 13th.**—Society of Arts, 4.30. "The Indian Mohammedans—Their Past, Present, and Future," by A. Yusuf Ali, M.A., &c.
- FRIDAY, 14th.**—Physical, 7. Exhibition of Electrical, Optical, and other Physical Apparatus.

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THE CHEMICAL NEWS.

VOL. XCIV., No. 2455.

ON THE ORIGIN OF JET.

By PERCY E. SPIELMANN, A.R.C.S., A.I.C., B.Sc. (Hons.) Lond.

It may be of interest to reconsider the question of the origin of jet in the light of some new observations made during the year in connection with petroleum and natural gas. Although jet is considered by many to be wood, waterlogged and subsequently highly compressed, the details of its formation do not seem to be satisfactorily accounted for, except in a single case. Dr. Gothan, of Berlin (a), presents a highly probable theory to account for the formation of jet from wood, but expressly states that it is not necessarily accompanied by bitumen, since there is no trace of the latter in the jet-bearing strata of Bornholm. Now, in Yorkshire the jet is accompanied by bitumen, natural oil, and gas; so much so, that jet is thought by many to be a mineral product formed by the segregation of bitumen from the surrounding rock. It is therefore of interest and importance to consider first the origin of bitumen and of petroleum.

Bitumen occurs in all gradations—from a mobile dark petroleum to a brittle shining black asphalt, from a slowly-flowing bituminous sand to a massive asphalt rock of considerable hardness. The purest specimen is found in the Dead Sea (b), into which it flows in fluid condition from neighbouring hot springs. In Trinidad it forms a great lake, surrounded by luxurious vegetation. Some of its properties may be gathered from Tables I. and II. (b).

TABLE I.

Locality.	Sp. gr.	Hardness.	M. p.
Bergteer of Lobsann, Lower Alsace	1	—	—
Bitumen from Trinidad ..	1.39—1.96	3	130—165°
Bitumen from Syria ..	1.103	3—4	135°
Bitumen from Maracaibo ..	1.091	3	130°
Bitumen from Barbados ..	1.041	2	110°

TABLE II.—Solubility.

	Water.	Dilute acids.	Caustic alkali.	Alcohol.	Ether.	Chloroform.	Petroleum.	Turpentine.
From Syria	Absolutely insoluble.	Absolutely insoluble.	Absolutely insoluble.	21 per cent	44 per cent	Completely soluble.	Completely soluble.	Completely soluble.
Trinidad	Absolutely insoluble.	Absolutely insoluble.	Absolutely insoluble.	5 "	57 "	Completely soluble.	Completely soluble.	Completely soluble.
Maracaibo	Absolutely insoluble.	Absolutely insoluble.	Absolutely insoluble.	Little "	Partly "	Completely soluble.	Completely soluble.	Completely soluble.
Barbados	Absolutely insoluble.	Absolutely insoluble.	Absolutely insoluble.	Partly	Partly	Completely soluble.	Completely soluble.	Completely soluble.
Pechelbronn, Lower Alsace ..	Absolutely insoluble.	Absolutely insoluble.	Absolutely insoluble.	Partly	Almost complete	Completely soluble.	Completely soluble.	Completely soluble.

Most specimens are completely soluble in CS₂ and C₆H₆.

Animal Origin.—Only the bare suggestion by Jaccard (c) in 1890, that bitumen is an animal product, as compared with petroleum being of vegetable origin, has been put forward under this head.

Mineral Origin.—Thorpe (h) does not consider bitumen to be produced by purely chemical means, for in that case it is to be expected that it would be of the same composition in the various localities in which it is found. But this is not so, as may be gathered from the analyses. An average analysis would give the following result:—

C	89.46 per cent
H	9.55 "
Ash	1.09 "
	100.10

Nitrogen and oxygen may be present, as in the Dead Sea bitumen:—

C	77.84 per cent
H	8.93 "
O	11.54 "
N	1.70 "
	100.01

Sulphur may be present to 10 per cent and mineral matter to 39.6 per cent (b). Out of twenty-seven analyses, thirteen have been found to contain oxygen, and eight sulphur (b). Although the flow of bitumen into the Dead Sea is increased after earthquakes, and is found mixed with sulphur (apparently confirming the Biblical account of the destruction of Sodom and Gomorrah), more recent examination has found no trace of vulcanity. On the contrary, the whole surrounding country seems to have been laid down in a quietly evaporating lake (b).

Vegetable Origin.—The bituminous dolomitic limestones of Lower Alsace contain a very large number of small fragments of wood, classified as coniferous wood (the very material that is considered to have given rise to jet). This limestone complex contains stalks, fruit, and leaves of *Chara Voltzi*, *Sabal major*, Cinnamomum, and Juglans, as well as Melania, Helix, Planorbis, and *Anthracotherium Alsaticum* (?). This is closely analogous to the Yorkshire jet rock, where wood, marine shells, and animal remains are found (b).

In Ragusa, Italy (b), occur rich fossil remains like stalks, apparently of the nature of plants, associated with which are sharks' teeth.

Peckham (b) considers the Trinidad asphalt to arise from the conversion of luxurious tropical vegetation to asphalt and then to bitumen by a low temperature distillation or fermentation.

On the whole the preponderance of evidence (both that cited above and that found in the literature of the subject) is in favour of a vegetable origin for bitumen, except in one case mentioned later on; so that even if some jet is formed from true bitumen (which is extremely unlikely, as will afterwards be seen) its origin still remains vegetable.

Petroleum always contains bitumen, just as bitumen always contains petroleum (b), and analyses show that both contain the same variable impurities, oxygen, nitrogen,

and sulphur, while gold and arsenic are sometimes found in addition in petroleum (d).

Animal Origin.—Zalozietki, 1897 (c), suggests that petroleum has resulted from the decomposition of albumenoid matter under the antiseptic action of the sea, since petroleum is connected with marine conditions. This is hardly correct, as petroleum is also found in peat bogs. Engler has also obtained an artificial petroleum by distilling animal fats at 10—20 atmospheres and 300—400° (b).

Mineral Origin.—Inasmuch as some of the members of the paraffin series have been obtained by the interaction of carbides and water, this mode of formation has been put forward for petroleum. This is possible, but, I think, very unlikely, owing to petroleum having been found recently to be optically active to polarised light.

Vegetable Origin.—Walden (c) has collected many measurements of optical activity of materials, animal and vegetable, connected with bitumen and petroleum, and finds the vegetable by far the largest in number and the more chemically probable. All the more so, as the animal substances are in general feebly active, while the vegetable resemble petroleum by being more strongly dextrorotary. This is strong evidence against the mineral theory of production of petroleum, since all substances which can be optically active, when produced by purely chemical means, are always inactive and have to undergo a subsequent process of separation into their active constituents; none of these can be thought to have occurred naturally in the case of petroleum.

Lesquereux (b) considers petroleum to have arisen from marine algæ; while the American experts suggest fucoids (b). Höfer (b) has found true fucoids in Pennsylvania and Carpathians, and in many other beds. From their experiments Krämer and Spilker (b) consider that algæ wax passes to ozokerite and then to petroleum, while Engler (b) suggests that animal fats decompose to bitumen and then petroleum, according to the conditions of pressure, temperature, and time. The unlikelihood of these latter theories will be seen shortly.

In all these suggestions one finds complicated bodies breaking down into more and more simple substances; but there is one where the opposite occurs. Strippelmann (b) contends that petroleum has hardened to asphalt. Many have found an asphalt-like substance from oxidising petroleum, also sulphur—which is often found in bitumens—polymerises petroleum, and Elchner (b) accounts for its presence by the reduction of local sulphates under great pressure. Clifford Richardson (b) has noticed that the hydrocarbons in bitumen have the general formula C_nH_{2n} , which can be easily polymerised at ordinary temperatures. One obtains also tarry matters when certain organic substances are treated with too violent reagents in the laboratory.

In spite of this, I think the gradual decomposition to simpler bodies to be the true direction of the change.

Natural gas is found both with or without accompanying petroleum, though its mode of origin must be very similar, if not actually identical.

In respect to the formation of bitumen and petroleum, one is tempted into assuming the agency of heat for an explanation by distillation (d, e), on account of the close resemblance to the distillation of coal giving oils and tar. But local examination of the deposits of bitumen and petroleum shows no trace of heat. The natural coke of Glasgow, Japan, and Sonora (Mexico), have no bitumen connected with them (b), and if petroleum were a distillation product, one would expect to find some degree of fractionation; this, however, does not occur (c). At the risk of being thought fashionable, I would suggest that these phenomena are not unconnected with radium or some other radio-active substance. Quite recently an announcement has been made by Drs. Cady and Macfarland, of the University of Kansas, that considerable quantities of helium have been obtained from the natural gas of Dexter and in less quantities from other natural gas fields. The radium here may have caused the particular decomposition by supplying the slow and continuous heat necessary, or it may have induced chemical decay; perhaps both effects occurred simultaneously. Assuming for the moment that jet is the woody remains left after the bitumen and petroleum and gas have gone, a further decomposition may have gone in the jet, whereby decomposition was pushed to its uttermost (since the composition of jet closely resembles that of anthracite), and a little more gas and oil produced in the jet, which explains the fact that a specimen weighing 100 grs. of jet, yielded about 30.2 c.c. of gases at 100° (g). These consisted of:—

CO ₂	..	..	..	10.93	per cent
C ₄ H ₁₀	..	..	..	86.90	„
N	..	..	..	2.17	„

100.00

Thus, the general trend of opinion—except that of Strippelmann—seems to be towards bitumen, petroleum, and natural gas being decomposition products of more complex bodies, very probably vegetable; and it is justifiable to assume that the more advanced and complex the decomposition the simpler are the substances produced.

Whether this decomposition has been brought about by the action of some radio-active substance, or by bacteria (like those which have been found fossil in coal), there seems little doubt that salts are closely connected with it, more especially aluminium salts. Natural gas and petroleum are very frequently associated with brine, and are probably generated from marine algæ and fucoids. The Dead Sea (b) contains aluminium salts, and the Dax salt (h) is close to a bitumen deposit. The shale above the Jet Rock in Yorkshire was formerly worked for the aluminium sulphate it contained; this is also obtained profitably from the coal measure shales near Manchester, and at Goole in Yorkshire, while aluminium mellitate (honey stone) occurs in peat bogs. It would thus seem that the aluminium sulphate has exerted the antiseptic influence known to be possessed by alum (i), thus retarding a bacteriological decomposition. Whether this salt could modify a decomposition caused by a radio-active substance cannot as yet be said.

Having shown that the three substances most closely connected with Yorkshire jet are highly probably vegetable in origin, it remains to consider the main subject—jet.

The best jet occurs in a particular horizon in the *serpentinous* zone of the Upper Lias Shale, but is never found in large pieces, the largest being 6 ft. 4 in. by 4 ft. 5 in. to 5 ft. 5 in. by 1 ft. 5 in., weighing 11.5 lbs. (g).

It varies considerably in quality, which is easily explicable on the assumption that the jet partially changed to bitumen and some petroleum, and that the latter evaporated, leaving a hard black deposit of inferior jet. So that one cannot say that this jet consists of bitumen or of wood—it is a solidified stage of the infinite gradations between true hard “wood jet” and “pure” bitumen.

That petroleum is present cannot be doubted on entering any of the old jet workings; the smell is strong, and inflammable gas has been met with in the old mines.

Bower (k) says:—“In one of the best specimens that has been found here, the mass in form and structure was that of a tree, with bark, knots, and roots, and in the curled portions of the roots, stones and soil conglomerated were imbedded.” Such an observation could hardly be imaginary, and is a most definite example to be advanced against the “bitumen” theorists.

In my own possession is a specimen of Spanish jet (closely resembling the Whitby jet), which has a perfectly straight even line of pyrites along one face, which has apparently been laid bare by a blow. Mr. Arber, of the British Museum, has been kind enough to examine it for me; he writes:—“Yes; I think part of the Araucarian wood has been replaced by pyrites, which thus conforms to the original structure. Under the microscope one seems to see markings as of the pits of the woody elements. Such specimens are rare but not unknown.” It is of interest also, as I have been assured by Mr. Newbitt, the curator of the Whitby Museum, and by a jet worker of thirty years' experience, that everything of an identifiable nature—fossil plants and shells, pyrites, &c.—in connection with jet, has been found *on* the jet and not *in* it.

In most specimens jet has been found to have lost almost all structure, but those in which it has been found have had their woody structure identified. And in some specimens where partial fossilisation has occurred, jet has formed that part of the wood unpreserved by the substituting materials.

Dr. Gothan (a), who, in the main, follows Prof. Seward, has made the following observations:—Wood in a sandy grey clay in Hermsdorf (Berlin) was allowed to dry in the open air. It was found to shrink greatly and twist spirally. It became very compact, being scarcely able to be cut with a knife, and under the microscope was found to have lost

almost all structure. This resulting material even developed certain zigzag lines, unexplained by Seward (l), but reproduced in fresh wood by Gothern by pressure, showing them to be the crumpled rings of growth of the original wood. Thus a substance well on the way towards resembling jet was formed even without pressure.

Those specimens of jet which have yielded traces of wood structure to the microscope have been found to be coniferous (Araucarian) (l), (g), (m). This wood also has given rise to the jet of Spain; it is found in the island of Bornholm and the wood associated with the bitumen of Lower Alsace is coniferous. A striking observation has recently been made by Mabery and Quayle (n) that Canadian petroleum probably contain terpenes.

It would seem from the manner in which jet occurs that coniferous wood has been washed from the land and become buried in the slowly depositing mud. A peculiar decomposition has set in which has been retarded or otherwise modified by the presence of salt water, and by the time the wood and oily matters have begun to break down, the mud had become sufficiently thick to form an impervious layer. As time went on and pressure increased, first from the weight of mud above, and then from the subsequent drying of the whole bed, the breakdown became more and more complete, helped by any heat which was probably generated in the decomposition. Not only was all air excluded, but strong reducing action occurred, causing the formation of a considerable amount of pyrites.

Substances sometimes resembling jet occur in lenticular masses in the Lower Lias clays of Dorsetshire, Gloucestershire, Leicestershire, and Shropshire (o); while in the Kimmeridge clay, also, jet-like substances are found (p).

But what happens, it may be asked, when vegetable matter is deposited in a sand instead of a mud? This can be seen in the Inferior Colite of Yorkshire, the Estuarine Sandstones. Here plant remains, and wood have decomposed in a comparatively porous bed; air dissolved in water could reach the vegetable matter more easily, decomposition would be more rapid and thorough, all the more so as the conditions are here estuarine and not purely marine, so that the water would not be so salt, and so allow a still more rapid decomposition. More oils and gas would be formed than bitumen, and these would escape and leave no trace. Considering these conditions are half way between those controlling the formation of jet and of coal, one would expect these Estuarine products also to be between the two; this is exactly what has happened. The literature speaks indiscriminately of this substance as "coal" or "soft jet" (q), (g), (i); an experienced jet-worker at first pronounced it to be soft jet, and then wondered if it could be coal; and on trial the degrees of polish of the three substances, jet, Estuarine soft jet, and coal, were graded in the right direction.

When, however, decomposition takes place in the lagoons and swamps of the carboniferous period, or the peat bogs of to-day, the amount of petroleum is small and that of the gas considerable. But as soon as shale becomes associated with these decompositions, as in the oil shales of Scotland, petroleum and bitumen are at once formed, for the double reason of the imperviousness of the bed and the prolonged decomposition of the original substances.

The above suggestions as to the origin of jet and bitumen from coniferous wood will account for all the apparent difficulties felt concerning the specimens in the Whitby Museum, as well as explain why all fossils, &c., are on the jet and not in it; and, furthermore, why no mud sand, &c., is found in the jet, as would have happened if the latter had consisted of bitumen segregating process obviously different from the segregation of flint.

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- (c) KLEMENT, *Bulletin de la Société Belge de Géologie*, 1897.

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- (e) *Chem. Zeit.*, 1906, xxx., 391, 1170.
- (f) QUENSTEDT, see KÖHLER, *supra*.
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- (l) SEWARD, "Jurassic Flora." Part II.
- (m) ABER, Mr., Note from.
- (n) *Am. Chem. Journ.*, 1906, xxxv., 404-432.
- (o) WOODWARD, H. B., "Jurassic Rocks of Britain." Vol. III. Lias of England and Wales (excluding Yorkshire), 1893.
- (p) TATE and BLAKE, "Yorkshire Lias," 1876.
- (q) "Encyclopædia Britannica," articles, "Jet," 1880; "Mineralogy," 1878.

THE USE OF THE ROTATING CATHODE FOR THE ESTIMATION OF CADMIUM TAKEN AS THE SULPHATE.*

By CHARLES P. FLORA.

(Concluded from p. 276).

VI. In Solutions containing Oxalates.

MUCH work was expended upon the oxalate method, but in spite of this, a satisfactory deposit could not be obtained. When ammonium oxalate was present, even in small amounts, the deposit was very spongy; while the use of sodium oxalate alone, when carried down even to the smallest excess possible to give a soluble double oxalate, gave results much too high. The dissolving of the precipitated oxalates in various reagents furnished no solution to the problem.

The results in Table VI. will show the scope of the work done. Of these, Nos. 1, 2, 3, 6, 8, 9, 14, 15, 17, and 18 gave very spongy precipitates, while No. 7 was so spongy that it could not be satisfactorily dried, and so was not weighed. In experiments numbered 4, 9, 10, 14, 15, and 18 the cadmium was not all precipitated in the time allowed. In No. 10, also, the precipitate was non-adherent. In No. 16 the oxalate was precipitated and was not broken up by the current.

VII. In Solutions containing Urea, &c.

Balachowsky (*Comptes Rendus*, 1900, cxviii., 385) obtained good results by the electrolysis of solutions containing, in addition to cadmium salts, urea and various aldehydes. These solutions were found to offer no difficulties with the rotating cathode, when cadmium sulphate is taken, as may be seen from Table VII. The deposits were grey, compact, and quickly dried. The solution was diluted to about 60 c.c. or 70 c.c., and the best current potential was found to be that given by six storage cells connected in series—approximately 11.8 volts.

Since the conductivity of the solutions containing urea and the aldehydes is comparatively low, the effect of adding electrolytes was tried. The rate of deposition was very much increased, but the precipitated metal showed such tendency towards sponginess that this procedure is not to be highly recommended. The tests tried are given in Table VIII.

VIII. In Solutions containing Formates.

The use of the solutions containing potassium formate and a slight excess of formic acid has been recommended (Warwick, *Zeit. Anorg. Chem.*, 1892, i., 285; Avery and Dales, *Journ. Am. Chem. Soc.*, 1897, xix., 380), but I was unable to adopt this method to the rotating cathode.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, xx., p. 268.

TABLE VI.

No.	Cd taken. Grm.	Ammonium oxalate, Grm.	Potassium oxalate, Grm.	Solvent.	Current = Ampères.	N.D. ₁₀₀ . Ampères.	E.M.F. Time. Volts. Mins.	Cd found. Grm.	Error. Grm.
1.	0.1491	Excess	None	None	3.0	9.0	12 ?	0.1558	+0.0067
2.	0.1491	Slight excess	None	None	2.5	7.5	12 30	0.1506	+0.0015
3.	0.1491	2.0	0.5	None	2.0—2.5	6.0—7.5	8 25	0.1531	+0.0040
4.	0.1491	None	0.5	15 drops H ₂ SO ₄	2.5	7.5	8 30	0.1476	-0.0015
5.	0.1491	None	8.0	None	2.0	6.0	6.2 20	0.1507	+0.0016
6.	0.1118	4.0	None	None	1.5	4.5	6.1 20	0.1272	+0.0154
7.	?	None	5.0	Few c.c. NH ₄ OH ₃	2.0—3.5	6.0—10.5	6—8 18	?	?
8.	0.1118	None	5.0	None	1.5	4.5	6.0 15	0.1129	+0.0011
9.	0.1019	None	4.0	None	2.0—3.0	6.0—9.0	8 20	0.0995	-0.0024
10.	0.1019	None	6.0	None	0.5—1.5	1.5—4.5	4—6 35	0.0982	-0.0037
11.	0.1019	None	5.0	None	1.0	3.0	5.5 55	0.1033	+0.0014
12.	0.1019	None	7.0	None	0.5	1.5	4 55	0.1030	+0.0011
13.	0.1223	2.0	8.0	None	0.1—0.15	0.3—0.45	4 60	0.1236	+0.0013
14.	0.1223	2.0	8.0	None	0.02—0.10	0.06—0.3	4 76	0.1229	+0.0006
		KOH.	H ₂ SO ₄ (dil.).	Oxalic acid.					
15.	0.1223	1.0	10 c.c.	5 grms.	3.0	9.0	8 40	0.0876	-0.0347
16.	0.1223	0.25	—	10 "	—	—	—	—	—
17.	0.1019	—	—	1 "	1—2	3—6	8 35	0.1033	+0.0014
18.	0.1019	—	—	3.5 "	3	9	8 60	0.1018	-0.0001

TABLE VII.

No.	Cd take Grm.	Current = Ampères.	N.D. ₁₀₀ . Ampères.	Time. Minutes.	Cd found. Grm.	Error Grm.
<i>Series A.—Urea, 3 grms.</i>						
1.	0.1019	0.25—0.5	0.75—1.5	35	0.1018	-0.0001
2.	0.1223	0.2	0.6	35	0.1223	0.0000
3.	0.1223	0.25—0.5	0.75—1.5	30	0.1230	+0.0007
<i>Series B.—Formalin, 2 c.c.</i>						
1.	0.1019	0.1—1.0	0.3—3.0	30	0.1018	-0.0001
2.	0.1223	0.2—1.0	0.6—3.0	30	0.1224	+0.0001
3.	0.1223	0.2—1.0	0.6—3.0	30	0.1225	+0.0002
<i>Series C.—Acetaldehyde, 2 c.c.</i>						
1.	0.1019	0.1—0.8	0.3—2.4	35	0.1022	+0.0003
2.	0.1223	0.1—0.8	0.3—2.4	30	0.1228	+0.0005
3.	0.1223	0.1—0.8	0.3—2.4	30	0.1222	-0.0001

TABLE VIII.

No.	Cd taken. Grm.	Electrolyte.	Cd found. Grm.	Error. Grm.	Notes.
<i>Series A.—Urea, 3 grms.; Time, twenty minutes; E.M.F., 7.8 volts; Current read, 0.5 ampère; N.D.₁₀₀, 1.5 ampères.</i>					
1.	0.1019	0.5 gm. K ₂ SO ₄	0.1031	+0.0022	Spongy.
2.	0.1019	0.5 "	0.1031	+0.0022	Spongy.
3.	0.1019	5 drops H ₂ SO ₄ (1 : 4)	0.1023	+0.0004	Good precipitate.
4.	0.1019	5 " "	0.1027	+0.0008	Slightly spongy.
5.	0.1019	8 " "	0.1027	+0.0008	Slightly spongy.

Series B.—Formaldehyde (formalin), 2.5 c.c.; Time, twenty minutes; E.M.F., 7.9 volts; Current started at 0.5 ampère and rose to 1.0 ampère at the end of the process (N.D.₁₀₀ = 1.5—3.0 ampères). In each case the precipitate was good. Ten drops of dilute sulphuric acid were added to increase the conductivity of the solution.

1.	0.1019	0.1020	+0.0001
2.	0.1019	0.1019	0.0000

TABLE IX.

No.	Cd taken. Grm.	KCHO ₃ , sat. sol. C.c.	HOCHO. Grm.	Current = Ampères.	N.D. ₁₀₀ . Ampères.	E.M.F. Volts.	Time. Minutes.	Cd found. Grm.	Error. Grm.
1.	0.1019	2	—	1.0—2.0	3—6	8	17	Not weighed; precipitate blistered and dropped off.	
2.	0.1223	0.5	—	0.4	1.2	8	—		
3.	0.1223	0.5	—	0.4	1.2	8	—		
4.	0.1223	0.5	—	0.4	1.2	8	—		
5.	0.1223	—	15 drops	0.25—0.8	0.75—2.4	12	25	0.1228	+0.0005
6.	0.1223	—	15 "	0.25—0.8	0.75—2.4	8	25	0.1212	-0.0010
7.	0.1223	—	21 "	0.5—1.5	1.5—4.5	12—16	35	0.1202	-0.0021
8.	0.1019	—	1.5 c.c.	0.5—1.0	1.5—3.0	12	60	0.1022	+0.0003
9.	0.1223	—	1.5 "	0.4—1.0	1.2—3.0	12	55	0.1218	-0.0005

TABLE X.

No.	Cd taken. Grm.	Tartaric acid. Grm.	Current = Amperes.	N.D.100. Amperes	E.M.F. Volts.	Time. Minutes.	Cd found. Grm.	Error. Grm.
1.	0.1223	3	0.5—1.0	1.5—3.0	8	20	0.1212	- 0.0011
2.	0.1223	2	0.5	1.5	8	30	0.1216	- 0.0007
3.	0.1223	2	0.5	1.5	8	50	0.1215	- 0.0008
4.	0.1019	3	1.5	4.5	11.8	18	0.1022	+ 0.0003

When potassium formate was present in even the smallest amounts the precipitate was spongy, and non-adherent. From solutions containing formic acid alone, however, the metal is deposited in a satisfactory form, but only after long passage of the current. The results given in Table IX. will show the limit of applicability of the process, experiments numbered 8 and 9 seeming to represent the most desirable conditions.

In the experiments numbered 5, 6, and 7, the cadmium was not all precipitated in the time indicated, as was shown by testing the solution with hydrogen sulphide.

IX. In Solutions containing Tartrates.

Solutions containing ammonium tartrate were also tried, but failed to give satisfactory deposits, the deposit in each case being spongy. If the solution contain only tartaric acid, however, in place of its salts, fairly satisfactory results may be obtained, as shown by Table X.

Tests with hydrogen sulphide showed that the cadmium was not all precipitated in the tests numbered 1, 2, and 3, which were performed at a dilution of 70 c.c.; Experiment 4 was performed at dilution of 50 c.c. It will be noted that, as in the sulphate process, the last traces of cadmium are thrown out of the higher state of dilution only with extreme difficulty.

to the negative elements with which it enters into combination. A number of instances were adduced by Dr. Wilde of phosphorescence and radio-activity in inorganic and organic nature in support of this view. The transformation of the radium bromide emanation into helium by Sir W. Ramsay and Mr. Soddy has been fully confirmed by Himstedt and Meyer, Giesel, and others. As no suggestion has been made that elementary bromine was set free during the transformation, chemists are confronted with the fact that both bromine and radium are simultaneously transformed into helium. The author expressed his satisfaction on the confirmation of the views and previsions advanced in his former papers on the origin of elementary substances, especially in connection with the transformation of radium into helium, and the places assigned to these elements in his tables previous to their discovery. The transformation of radium combinations into helium clearly demonstrates that the "constitution of matter" is not necessarily atomic in the sense generally accepted by chemists. Dr. Wilde declared his conviction that the ultimate constitution of all substances, including the universal medium (ether) that fills infinite space, is absolutely inscrutable to human understanding. This conviction he shares with that distinguished cultivator of natural knowledge, Sir W. R. Grove, who in his epoch-making book on the "Correlation of Physical Forces" refers to "the harm done by attempting hypothetically to dissect matter, and to discuss the shapes, sizes, and numbers of atoms, and their atmospheres of heat and electricity." Not the least valuable result of the study of mental philosophy is the conscious realisation of its limitations.

ON SOME POINTS OF CHEMICAL PHILOSOPHY INVOLVED IN THE DISCOVERY OF RADIUM AND THE PROPERTIES OF ITS COMBINATIONS.*

By HENRY WILDE, D.Sc., D.C.L., F.R.S.

DR. WILDE referred to the profound interest created by the discovery of the new element radium, as evidenced in various scientific publications and in magazine articles on "The Revelations of Radium," "The Miracle of Radium," and other titles equally striking. Although the new element has not yet been isolated, its spectrum and chemical reactions leave no room for doubt of its existence. He discussed the series-position, atomic weight, and specific gravity of radium as prevised in his former papers published some years before its discovery, and gave reasons for retaining the values then assigned to them in his tables. It was pointed out as a singular circumstance that, notwithstanding the wonderful powers attributed to radium, no chemist has yet seen or handled the element in its pure metallic state, in order that its general properties might be ascertained. Reference was made to the undisputed fact that all the elements of the series containing radium, which exhibit the property of phosphorescence and radio-activity when in combination with sulphur or other electro-negative elements, behave like ordinary substances when in the elementary metallic state. By strict analogy metallic radium would, in like manner, be divested of all the extraordinary properties which have been attributed to it and opened out so wide a field for ultra-scientific hypotheses. Moreover, as the phosphorescent properties of the radium series only become manifest when in combination with the chlorine and oxygen series of elements, it may with good reason be maintained that the extraordinary properties attributed to radium really belong

HYDROXYLAMINE- $\alpha\beta$ -DISULPHONATES.*

STRUCTURAL ISOMERIDES OF HYDROXIMINO-SULPHATES
OR HYDROXYLAMINE- $\beta\beta$ -DISULPHONATES.

By TAMEMASA HAGA,
Professor of Chemistry, Imperial University, Tokyo.

(Concluded from p. 279).

Decomposition of the Potassium Salt by Potassium Hydroxide.

WHETHER potassium hydroxylamine- $\alpha\beta$ -disulphonate is decomposed solely into acid-sulphate, aminemonosulphonate, and nitrogen, when heated with a concentrated solution of potassium hydroxide (see *ante*), or whether it is, to a small extent, decomposed into nitrous oxide, according to the equation—



is not certain. It is experimentally difficult to get sufficiently trustworthy qualitative results. Even qualitatively, there is the uncertainty to deal with, as to the entire absence of nitrous oxide from the nitrogen obtained. In these experiments, the gas given off extinguished a flaming match and refused when mixed with hydrogen to explode by the electric spark. The occasional production of some nitrous oxide is, perhaps, to be inferred from the ratio of the quantity of sulphur as sulphate to that as aminemonosulphonate found in one experiment, although its production was not thus indicated in another experiment. But,

* Read before the Manchester Literary and Philosophical Society, November 27th, 1906.

* Journal of the College of Science, Imperial University, Tokyo, Japan, xxi., Article 6.

as accuracy in determining this ratio is affected by the fact that the analytic separation of sulphate from aminemonosulphonate is only approximate (*Journ. Coll. of Sci., Japan*, ix., 281; xiii., 503), the production of any nitrous oxide still remains uncertain. Another difficulty in the quantitative examination of the decomposition is that the decomposition is far from complete after several hours heating at 120°. The presence of still undecomposed salt is shown by the production of hydroxylamine when the products are hydrolysed and by the fact that a temperature of 180°, instead of 150°, is necessary to ensure complete hydrolysis of the products. No ammonia is generated, the only products being those already mentioned.

When the gases were to be collected the salt was heated with one and a-half to twice its weight of potassium hydroxide and about four times its weight of water for six hours at 100° or for four hours at 120° in a tube retort connected with a Sprengel pump. Needless to say, explosive ebullition and corrosion of the hard glass tube (rendering it opaque) had to be encountered as difficulties. When the gases were to be allowed to escape, the mixture was heated in a platinum dish on the water-bath. For analysis, the residue in either case was made faintly acid to phenolphthalein by nitric acid, and sulphate then precipitated by barium nitrate. The thoroughly washed precipitate was purified in the usual way by fusion with an alkali carbonate before weighing. The aminesulphonate was precipitated by mercuric nitrate, the mercuric salt was hydrolysed, and the sulphuric acid and sometimes the ammonia resulting were determined. The filtrate from the mercury precipitate always showed the presence of hydroxylamine-*αβ*-disulphonate.

In an experiment with 1.057 grm. of salt, the sulphur found as sulphate was 66.82 per cent, and that as aminesulphonate 15.73 per cent of the total sulphur, leaving 17.45 to be accounted for as undecomposed salt. Of the total nitrogen, 29.64 per cent were got as ammonia from the aminesulphonate, and 48.89 per cent as gas (27.85 c.c. moist nitrogen at 18° and 639.8 m.m. = 0.002692), leaving 21.47 per cent as undecomposed salt. The difference between 17.45 and 21.47, perhaps due to slight leakage of air into the apparatus during the six hours heating, is not at all so significant as it is made to appear by the way of stating the results, the total percentage of nitrogen in the salt being only 5.2 per cent. On the assumption that 65 per cent of the salt decomposed so as to give nitrogen (see *ante*) and 16.7 so as to give nitrous oxide (see above), and that 18.3 per cent remained undecomposed, the numbers should be sulphur as sulphate, 66.68, and as aminesulphonate, 15.01 per cent, nitrogen as aminesulphonate, 30.02, and as free nitrogen and nitrous oxide, 48.30 per cent of the total.

In another experiment, in which 0.9792 salt was heated at 120–125° for four hours, the indications of the analysis were that 19.9 per cent of the salt had resisted decomposition and that no nitrous oxide had been formed. The numbers obtained were 66.69 per cent sulphur as sulphate, instead of 66.75 calculated; and 12.94 sulphur as aminesulphonate, instead of 13.35 calculated. Some of the gas was lost, so that the distribution of the nitrogen could not be sufficiently tested.

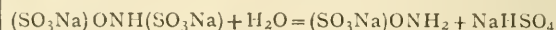
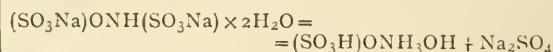
In an experiment in which the salt was heated at 100° with potassium hydroxide for many hours in a platinum dish with occasional renewal of the water, the sulphur of the sulphate produced amounted to 77.24 per cent of the total. Decomposition of all the salt with production of nitrogen would give 83.33 per cent.

Products of Hydrolysis of Hydroxylamine-*αβ*-disulphonates.

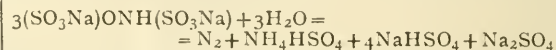
Potassium hydroxylaminetrisulphonate, which for these experiments could be substituted for the disulphonate, the product of its hydrolysis, was moistened with dilute sulphuric acid and heated in a vacuum at 100°, in order to effect its hydrolysis and collect the gas evolved. The gas had no action upon ferrous sulphate, and was not appreci-

ably soluble in alcohol. It therefore contained no nitric oxide and apparently no nitrous oxide.

Sodium hydroxylaminetrisulphonate in solution in water, just acid with sulphuric acid, was left for several days to slowly hydrolyse, principally to the disulphonate. It was then kept for fifty minutes at 95°, during which brisk effervescence of nitrogen went on, slackening only when near the end of the time. The acidity was then found to be somewhat more than that indicated by either of the following equations, the one for hydroxylamine sulphate, the other for the unknown hydroxylamine-*α*-monosulphonate:—



The additional acidity and the escape of nitrogen indicated the occurrence, to some extent, of the decomposition expressed by:—



The solution gave only a moderate reaction for hydroxylamine with the copper test, and on evaporation, with or without previous neutralisation, gave nothing but sodium and ammonium sulphates.

In presence of sufficient hydrochloric acid, say, one volume of the fuming solution to ten volumes of solution of the salt, the production during hydrolysis of nitrogen and ammonia is very slight. The disodium salt in such a solution, after it had been kept heated for five minutes or so by immersing the vessel in boiling water, gave evidence, on titrating with iodine, of the presence of hydroxylamine equivalent to 95 per cent of the salt. In another experiment, in which the solution was left standing for 50 days at the ordinary temperature, 76.5 per cent of the salt had then yielded hydroxylamine.

In another similar experiment, the solution after standing in the cold was also evaporated in the cold under reduced pressure, until the salts crystallised out, and still nothing else but sodium and hydroxylamine sulphates, except a very little ammonium sulphate, was obtained.

In other experiments, using in these cases the dipotassium salt, the hydrolysis was allowed to go on either in the cold or at 60°, and portions of the solution occasionally tested to see whether some indication could be got of the production of hydroxylamine-*α*-monosulphonate at any stage of the hydrolysis. In making the test, the acid sulphate was removed by barium chloride and the solution then tested with iodine in presence of sodium acid-carbonate. Since the consumption of the iodine caused no precipitation of barium sulphate, evidence was thus obtained that the reducing substance was hydroxylamine only and not its sulphate derivative. Ultimately, by evaporating the solution, when sufficiently hydrolysed, hydroxylamine sulphate was crystallised out, along with the sodium sulphate.

Separation of Chlorine and Bromine in Acid Solution with Hydrogen Peroxide.—P. Jannasch.—The quantitative separation of bromine and chlorine by means of hydrogen peroxide in solutions containing sulphuric acid is dependent upon the concentration of the acid. If the solution contains too little acid the bromine is only partially isolated, and in very dilute solutions the reaction practically does not occur. If, however, much sulphuric acid is present the bromine separates out even in the cold. It is best to heat the mixture of halogens in a current of carbon dioxide. The method is then very accurate, although the bromine found was always a trifle low, owing to slight defects in the arrangement of the apparatus, mechanical loss, &c. No trace of bromide ever remained behind with the chloride.—*Berichte*, xxxix., No. 14.

PROCEEDINGS OF SOCIETIES

PHYSICAL SOCIETY.

Ordinary Meeting, November 23rd, 1906.

Prof. J. PERRY, F.R.S., President, in the Chair.

A PAPER on the "Electric Radiation from Bent Antennæ" was read by Dr. J. A. FLEMING, F.R.S.

The author referred at the outset to a paper read to the Royal Society in March last by Mr. Marconi on "Methods whereby Electric Waves may be mainly confined to certain directions," and to his own note read at the same time and published in revised form somewhat later on, "The Theory of Directive Antennæ or Unsymmetrical Hertzian Oscillators" (*Proc. Roy. Soc.*, 1906, A, vol. lxxviii., p. 1). Mr. Marconi showed that if a vertical radiator earthed at the lower end was bent over so that a short part was vertical and a much longer part horizontal, it radiated less vigorously in the direction in which the free or insulated end pointed than in the opposite direction. He (Dr. Fleming) had shown mathematically that this difference depended upon the ratio of the wave-length of the radiated wave to the distance between the radiator and receiver, as well as upon the ratio of the lengths of the horizontal and vertical parts of the antenna. Mr. Marconi had operated with waves of about 150 metres wave-length, but it appeared desirable to test the theory and the expressions given by the author for the electric and magnetic force round such a bent antenna by making experiments with shorter wave-lengths and correspondingly shorter distances. The paper is accordingly occupied with an account of experiments made during the past summer in the quadrangle of University College, London, with radiating antennæ consisting of wires bent in various ways, which have the property of radiating electric waves more strongly in some directions than others. The receiving arrangement used was first described. It consisted of a thermoelectric oscillation-detector contained in a double test-tube like a Dewar vacuum-vessel as used for collecting liquid gases. Four copper strips pass down the inner tube, and platinum wires soldered to them are sealed through the glass. One pair of these are connected by a fine constantan wire about 0.02 m.m. diameter, and the other pair are connected by a tellurium-bismuth thermojunction which just touches the centre of the fine wire. A high vacuum is made in the space between the test-tubes. If electric oscillations are sent through the constantan wire and a suitable galvanometer connected to the thermojunction, this receiver affords a means of measuring the root-mean-square value of the oscillations induced in any receiving antenna when the fine wire is inserted between the antenna and the earth. The receiver used gave deflections almost exactly proportional to the square of the current passing through the fine wire. This receiver was inserted between an earth-plate and a vertical receiving-antenna consisting of a double copper wire 20 feet high with a small capacity-plate at the top. The transmitting antenna consisted of a similar wire and plate so supported that it could be bent over at any required height above the ground and the horizontal part swivelled round into various azimuths. Readings were taken of the current in the receiving antenna, and plotted out as polar curves corresponding to the various directions of the free end of the transmitter. Curves are given in the paper showing the form of the polar curve when the 20-foot transmitting wire is all vertical or bent over at a height of 1 foot, 2 feet, 3 feet, 4 feet, 5 feet, and 10 feet respectively from the ground, and these show that the intensity of radiation in various azimuths for constant distance between receiver and transmitter becomes more unequal as the ratio of horizontal to vertical part of the transmitter increases. Also all the polar curves show a minimum radius vector or radiation corresponding to a direction of the free end of the transmitter, such that it makes an angle of 70° to 75° with

the line joining the earthed points of the transmitter and receiver. This is shown to be entirely in accordance with the theory given by the author. For the case of a certain ideal small bent antenna partly vertical, partly horizontal, the magnetic force H at any distance r from the transmitter when sending out waves of length $\lambda = 2\pi/m$ taken in a direction such that r makes an angle θ with the direction in which the horizontal portion of the antenna points is given by the following expression:—

$$H = \frac{1}{r^2} \left\{ (\phi v m^2 r^2)^2 + (\phi v m r - \frac{M}{2} m^2 r^2 \cos \theta)^2 \right\}^{\frac{1}{2}},$$

H being the magnetic force at the end of the radius vector perpendicular to it and also parallel to the earth's surface. ϕ in the above equation is the electric moment of the antenna and M its magnetic moment.

This equation shows that H has a minimum value when—

$$\cos \theta = \frac{2\phi v}{M} \cdot \frac{1}{mr},$$

and it is shown in the Paper that for the cases considered—

$$\cos \theta = 0.375 \times \lambda/r,$$

The experiments were all made at distances r such that λ/r was nearly equal to 0.72, and hence the minimum value should occur when—

$$\cos \theta = 0.27 \text{ or } \theta = 74^\circ 20',$$

which is not far from 75° as actually found by observation. For the family of curves given show that the minimum radii occur at 105° reckoned from the direction opposite to that in which the free end points. It is shown that the form of the polar curve observed for the same sending antenna, but with different distances between sender and receiver, varies as it should do by theory. A large number of forms of antenna were examined, some consisting of a single bent wire and others of a vertical wire with a lateral attachment, and the polar curves are given showing the field at constant distance but in various azimuths round these transmitters. It is shown that if a double bent antenna was used consisting of a semicircle of wire with the ends of the two vertical parts bedded in the earth, the polar curve round it would be a simple Cosine Curve or figure-of-8. In the case of a simple vertical sending wire the polar curve is of course a circle. If a vertical radiating wire is therefore bent over so as to have part of its length vertical and part horizontal, its polar curve is of an intermediate form and is a sort of deformed oval or figure-of-8 curve with unequal loops always having a minimum radius vector at nearly the same vectorial angle of 70° or 75° reckoned from the longest diameter. The Paper concludes with an explanation of similar effects observed by Mr. Marconi in the case of bent receiving antennæ; and it is shown that these effects cannot be explained without admitting three sources of electromotive force in the bent receiving-antennæ—(i) that due to the magnetic force of the incident wave, (ii) that due to the electric force, and (iii) an electromotive force due to the periodic insertion and removal of lines of magnetic force from the nearly closed loop formed by the bent antennæ. Generally speaking, all the directive effects found to be associated with bent transmitting and receiving antennæ, as used for wireless telegraphy, are explicable on the basis of the theory expounded by the author in the above-mentioned mathematical paper. The important bearing of these facts and observations on the problem of directive electric wave telegraphy was also pointed out.

A paper was read by Dr. CHREE entitled "Auroral and Sun-spot Frequencies Contrasted."

In several recent papers the author has investigated the relationships between certain phenomena of Terrestrial Magnetism and Sun-spot Frequency. The present paper makes similar comparisons between Sun-spot frequency and the frequency of Auroras. The sun-spot data utilised are from the big table of Wolf and Wolfer, covering the long period 1749 to 1901, and containing mean values for

every month of that period. Mean values have been calculated from this table for each month of the year, employing the whole period and certain portions of it, and also dealing separately with years of many and years of few sun-spots. One object was to see whether there was appreciable variation in the mean sun-spot frequencies thus obtained for individual months of the year. The differences between the means for individual months proved to be by no means negligible when calculated from 33 consecutive years, or from groups of 33 or 39 years selected as representing sun-spot maximum and minimum. The uncertainties thus introduced into enquiries as to the variation throughout the year in the relationships between sun-spot frequency and terrestrial phenomena are pointed out.

A comparison is instituted between mean sun-spot frequencies and mean auroral frequencies calculated for the same group of years. The auroral frequencies are taken from two sources—viz., Catalog der in Norwegen bis Juni 1878 beobachteten Nordlichter zusammengestellt von Sophus Tromholt, herausgegeben von J. Fr. Schroeter; and Joseph Lovering's "On the Periodicity of the Aurora Borealis."

During the long periods dealt with, there seemed strong reason to believe that variation occurred in the unit of auroral frequency. To eliminate such uncertainties as far as possible, a period, say, poor in sun-spots is contrasted with two equal periods rich in sun-spots, one preceding and the other following it. An investigation is made as to whether the annual variation of auroral frequency is the same in years of many as in years of few sun-spots. The evidence is not perhaps altogether decisive, but so far as it goes it points to the conclusion that, *relatively* considered, the annual variation is more pronounced—i.e., the range a larger fraction of the mean value when sun-spots are few than when they are numerous. A similar phenomenon has been described by the author in the case of magnetic storms at Greenwich.

The parallelism between sun-spot and auroral frequencies is on the whole fairly similar, whether the auroral frequencies are derived from Lovering's General Catalogue or from the Tromholt-Schroeter data for Scandinavia as a whole. There seems, however, to be a somewhat conspicuous difference between the variation in the annual auroral frequencies derived from the South and the North of Scandinavia; and data which Danish observers have published for Greenland seem to indicate an inversion even of the relationship with sun-spots observed elsewhere. At first sight, the much greater length of time for which records exist suggests that Aurora lends itself more readily than Terrestrial Magnetism to a comparison with sun-spots; but this seems to be more than neutralised by the heterogeneous nature of auroral data.

Dr. J. A. HARKER asked if in making calculations upon sun-spot frequencies any account was taken of the different sizes of spots.

Dr. CHREE said the Astronomer Royal measured the areas of the spots, but Wolf used a "relative number" depending upon the total number of spots observed and upon the number of groups and isolated spots. The two methods of estimating the sun-spot frequency agreed well.

A paper was read by Dr. R. S. WILLOWS "On the Electrical Resistance of Alloys."

Lord Rayleigh has given a theory intended to account for the high resistance of alloys compared with that of the constituent metals (*Nature*, June, 1896, and Collected Papers, vol. iv., p. 232). According to this theory, when a current is sent through an alloy it sets up a series of Peltier effects at the junctions of the dissimilar metals, and hence also a back E.M.F. Since these effects are proportional to the current, they are indistinguishable from a resistance under ordinary conditions. It is this spurious resistance that may account for the difference in behaviour of an alloy and a pure metal. The author attempts to put this in evidence by measuring the resistance of an alloy with direct and also alternating currents. At the instant

of reversal of the latter the back E.M.F., will assist the external E.M.F., and hence more current will pass, i.e., the resistance will apparently be reduced. A bridge method is used, the frequency varying between 10—980 per second. No spurious resistance could be detected. If it were present its temperature coefficient would probably differ from that of a pure resistance. The method is therefore used between temperatures 100° C. and that of liquid air, but again with negative results. A minimum accuracy of 0.02 per cent is attained.

Prof. J. A. FLEMING expressed his interest in the paper and said Lord Rayleigh's theory was ingenious, but it seemed to him that it pre-supposed a coarseness of structure in the alloy. An alloy was probably a substance of the nature of a solution with a fine structure, and it was difficult to see how thermoelectric E.M.F.s could be brought into play without discontinuity of material. Considering an electric current as a passage of electrons, Prof. Fleming pointed out that some of the electrons would pass through the spaces between the molecules in the material and others would impinge against the molecules themselves or the molecular aggregates. The latter would set up perturbations which would produce heat and corresponding electric resistance. If an alloy were supposed to consist of molecular aggregates while a pure metal consisted of molecules, more electrons would pass through material in the latter case than in the former. This would produce a greater quantity of heat, and correspond to a higher resistance in the case of the alloy.

Mr. A. CAMPBELL said that shortly after Lord Rayleigh advanced his theory he made some experiments to try to detect if alloys showed changes of resistance when tested with alternating and direct currents. The alloy selected was ferro-nickel, as it was expected that this would show the effect strongly, as the constituents give a strong thermoelectric E.M.F. A current was sent through a long ferro-nickel wire doubled back on itself, and this current was measured by a Kelvin balance, while the voltage on the ends of the wire was measured by a Kelvin electrostatic voltmeter (reading to 1 in 1000). No difference could be detected between the apparent resistance with direct current and with alternating current of frequencies up to 80 per second (the usual correction for contact difference being found and applied).

Mr. W. DUDELL suggested that the author should proceed with his experiments using very much higher frequencies.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, December 3rd, 1906.

Dr. J. LEWKOWITSCH in the Chair.

"The Direct Estimation of Antimony," by H. W. ROWELL.

The sample of finely powdered ore or fine metallic sawings containing about 0.14 gm. of antimony is weighed into a 500 c.c. beaker, and dissolved in 25 c.c. of strong hydrochloric acid. Five c.c. of saturated solution of bromine in hydrochloric acid are run in, and any insoluble matter is fused in caustic soda and returned to the main bulk. Three grms. sodium sulphite are added, and the mixture boiled down to 10 c.c. to drive off sulphurous acid and arsenic. The solution is titrated at a boiling temperature, after the addition of 60 c.c. of hydrochloric acid (1 to 3), with N/20 potassium bromate until the colour of the methyl orange indicator is destroyed. The bromate is standardised with 0.082 gm. of arsenious oxide dissolved in hydrochloric acid, which is equivalent to 0.1 gm. of antimony. Copper raises the result slightly and iron very slightly, but precautions are given for obviating their effect.

The method may be applied to materials containing antimony, and examples are given illustrating the accuracy

of the method, the effect of copper and variations in samples of alloys.

"The Standardisation of Disinfectants." By M. WYNTER BLYTH, B.A., B.Sc., F.I.C.

The present paper records the results of a number of tests made with disinfectants in the presence of organic matter which tend to prove that organic matter influences the efficiency of disinfectants to an enormous extent. In the Rideal-Walker test the possible influence of organic matter was not considered. Faeces, urine, blood, and milk all influence the carbolic acid coefficients (*i.e.*, the dilution of a disinfectant which kills a given organism in a given time, divided by the dilution of carbolic acid which kills the same organism in the same time) of the majority of the disinfectants examined. There are, however, a few disinfectants, such as formalin and chinolol, which do not appear to be influenced by the presence of organic matter.

With emulsified tar oils the drop in coefficient on the addition of small quantities of certain organic matter is very great, but as more and more organic matter is added the drop becomes proportionately less until the coefficient is constant.

The particular types of organic matter which influence the coefficient to the greatest extent are fat and proteids; carbohydrates and bile soaps having little or any influence.

The coefficients in faeces lie between those obtained in separated milk and in whole milk. Faeces of any given composition may be imitated by taking milk of suitable richness in fat and proteids.

With oxidising disinfectants the drop in the coefficient obtained is proportional to the time during which the disinfectant and organic matter are allowed to remain in contact before adding the test organism. If, however, the organism is first added and then the disinfectant, the drop in coefficient is proportional to the oxidisable organic matter present, and may be represented by a straight line. It is pointed out that the organism used has a great influence on the coefficient obtained, a matter of importance when the coefficients are used for commercial purposes. As a general rule, it has been found that the higher the resistance of the organism is to carbolic acid the lower is the coefficient obtained for other coal-tar disinfectants.

Experiments are recorded on various strains of organisms of the coli group which show the importance of determining the cultural characteristics of any organism used, as different strains may give very different results. A modified thread method is suggested, and results are given which show that disinfectants containing soaps have considerably higher powers of penetration than is indicated by the ordinary thread method.

As a result of the author's investigations it is suggested that the efficiency of disinfectants can only be indicated by a series of figures obtained in water and in organic matter, and by both the drop and the thread methods. Even then the figures so obtained are only applicable to the particular organism used.

"The Detannisation of Solutions in the Analysis of Tanning Materials." By Dr. J. GORDON PARKER and H. GARNER BENNETT, B.Sc.

The authors deal with the four chief methods used for the analysis of tanning materials and extracts, and compare the official method of the International Association of Leather Trades Chemists, which consists of detannisation by means of a column of prepared hide-powder in a specially made filter-bell, with the German method, with the method devised by Kopecky, and finally with the official American method.

The authors have carried out their experiments with materials of standard strength, using pure gallotannic acid, to which they have added various substances other than tannin, and show that such materials as glucose, dextrine, gallic acid, calcium acetate, and calcium lactate, sulphate of magnesia, salt, sodium bisulphite, and oxalic acid are all absorbed to a lesser or greater degree by hide-

powder, and are returned by the official method of analysis as tannins. The authors give results of some four hundred analyses, using gallotannic acid admixed in various proportions with the above named materials. The result of the work is a vindication of the claims of the American method.

The authors confirm the work that has been done by Reed and other American chemists, and disprove the claims made by Paessler that a dry chromed hide-powder used in the filter-bell gives the most accurate results. The authors finally recommend that the International Association of Leather Trades Chemists should at once adopt the American method, either as it now officially stands or in a modified form.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 22, November 26, 1906.

Alcoholysis of Cocoa-butter.—A. Haller and M. Yousoufian.—The fatty matter of cocoa has been the object of much research since the first investigation of it by Trommsdorf, published in 1815. Its importance as a food substance and the difficulty of freeing it from the butter and other natural fatty substances with which it occurs, add to the interest of the researches spent upon it. But in spite of the numerous analyses effected, the authors have not yet arrived at a unanimous statement of its constitution; *e.g.*, Ulzer doubts the presence of palmitine in this fatty substance, and Reyst finds in it neither palmitine nor stearine. Lewkowitsch, on the other hand, attributes to it the presence of both these glycerides together with those of caproic, caprylic, capric, lauric, myristic (the two latter in proportionately great quantity), and oleic acids. The authors of this article used for the alcoholysis the butter which is imported in considerably large quantities into Europe, and obtainable as such without transformation. The constants were determined and found to agree fairly well with most of the cocoa-butters described in chemical literature. The fatty substance was treated with absolute methyl and ethyl alcohols, according to the conditions mentioned in a previous note. In the final result the weight of ether salts obtained was equal to the weight of the fatty matter employed. Fractional distillation of the methyl-alcoholysis of the cocoa-butter yielded the caproate, caprylate, caprate, laurate, myristate, palmitate, stearate, and oleate of methyl. No butyric ether could be found in the mixture. In order to confirm the conclusion that cocoa-butters of different origin have the same composition as the commercial product analysed, experiments were made with other butters with the same result, and with no appearance of butyric. To sum up, cocoa-butters contain the glycerides of the saturated fatty acids corresponding to C₆, C₈, C₁₀, C₁₂, C₁₄, C₁₆, C₁₈, and of oleic acid, among which laurine and myristine predominate.

Improvement of the Eudiometer. Search for, and Estimation of, Carbon Monoxide.—Nestor Gréhaut.—The author describes in detail the means by which he has perfected the mechanism of the eudiometer. He has put it to a new use in the investigation, as yet incomplete, of poisoning by carbon monoxide. Certain experimenters and hygienists affirm that this gas, even in infinitesimal quantities such as 1/100000, may cause serious results in man, and to test this opinion a series of comparative experiments were performed. Three rabbits as similar as possible were made to breathe definite mixtures of carbon monoxide and air equal to 1/5000 and 1/10000 for one hour, five hours, and nine hours respectively. Hæmoglobin is the best

absorbent of carbon monoxide; the gas was then extracted from the blood, to which tri-hydroxy-phosphoric acid was added, with the mercury pump, and the following results obtained. 100 c.c. of blood contain in c.c. of carbon monoxide:—

	Mixture 1/5000.	Mixture 1/10000.
At the end of 1 hour ..	2'2	1'12
" " 5 hours ..	3'1	1'42
" " 9 " ..	3'1	1'43

These results are of the greatest importance; they prove that for small proportions of carbon monoxide the figures of the gas absorbed by the blood at the end of five hours and at the end of nine hours are identical; there is therefore in the curve of the results obtained a horizontal resembling that which the author has discovered in his researches upon alcohol poisoning.

A Method of Preparing Hydrated Hypovanadic Acid.—Gustave Gain.—The author has succeeded in preparing on a large scale this body, which hitherto has been obtained with difficulty. The starting-point is the metavanadate of ammonia, which on heating in a crucible is transformed into a deep blue powder, a mixture of V_2O_3 and V_2O_4 . This, after heating for several days with a saturated solution of sulphurous anhydride, became a beautiful azure-blue colour, part of the dark blue powder being transformed into a light blue body consisting of fine needles, a sulphite of V_2O_4 , which on analysis pointed to the formula $2V_2O_4 \cdot 3SO_2 \cdot 10H_2O$. A certain quantity of the azure-blue liquid was then gently heated, causing, first, evolution of SO_2 , and, finally, deposition of a fine crystalline powder. This deposition increased with slow prolonged cooling. Analysis of the crystals gave the formula $V_2O_4 \cdot 2H_2O$. From this hydrate a certain number of salts of hypovanadic acid were also obtained.

Research upon the Elements producing Phosphorescence in Minerals. The case of Chlorophane, a Variety of Fluorite.—G. Urban.—The author has previously described most of the phosphorescences observable on submitting to the action of the cathode rays, mixtures of pure chalk with the pure oxides of the different rare earths. By this method traces of bodies are detected which would by any other method escape unnoticed. The same method is now applied to certain phosphorescent minerals, in particular to some fluorites, which manifest this property in high degree. The chemical causes of the phosphorescence of fluorites had not yet been experimentally investigated. Chlorophane, the most remarkable of the varieties of fluorite, emits on heating a beautiful greenish-white light (whose spectrum H. Becquerel has described). The bands, easily observable in the cathode region, appeared to indicate that the phosphorescence of chlorophane was due to rare earths, and this the author has proved to be the case, both by analysis and synthesis. By the method of analysis the fluoride was transformed into oxide. After comparisons of various spectra, traces of the following elements were detected in chlorophane:—samarium, terbium, dysprosium, and gadolinium. A partial synthesis of the phosphorescent fluorites was necessary for the further definition of the phosphorescent element of chlorophane. The fused amorphous precipitated fluorides were used. By this means, the different bands of phosphorescence of chlorophane were properly ascribed to the corresponding rare earths, already indicated by spectrum analysis.

Transformation of Cinnamic Alcohol into Phenyl Propylene and Phenyl Propylic Alcohol by the Ammonium Metals.—E. Chablay.—Previous experimenters have, by the action of nascent hydrogen upon cinnamic alcohol, converted it into phenyl propylene and phenyl propylic alcohol. The author gets the same result by the action of sodammonium upon cinnamic alcohol. A clear, yellow solid substance results, which is decomposed by water, dissolved in anhydrous ether, and submitted to fractional distillation. A phenylpropylene was isolated, of

the formula $C_9H_{10}Br_2$, between 165° and 170° . Phenylpropylic alcohol was obtained from rectification of the fractions distilling at 235° to 250° , it being a liquid distilling at a constant temperature at 236 – 237° . Analysis gave it the formula $C_9H_{12}O$. Oxidation with chromic acid in acetic acid solution transformed it into phenylpropionic acid, $C_6H_5-CH_2-CH_2-COOH$, fuzing at 47.5° . The alcohol is a thick, colourless liquid, with an agreeable flowery odour. The experiment proves that the metallic ammoniums reduce cinnamic acid, just as they reduce the non-saturated alcohols of the fatty series to give the corresponding carbide, and with similar working. But the reduction is the minor part of the reaction, the principal result being the formation of phenylpropylic alcohol.

Préparation of the Oxynitriles $ROCH_2CN$.—D. Gauthier.—The author starts with the monochlor ether oxides, $R-O-CH_2Cl$. In these compounds, treated with mercuric cyanide, or preferably with cupric cyanide, the group CN easily replaces Cl, and furnishes a new series of compounds, $R-O-CH_2-CN$. Of this, only one term was already known, viz., the oxynitrile, $C_2H_5-O-CH_2-CN$, being prepared by dehydrating the corresponding amide by means of phosphoric anhydride, but the author's method yields also methyl, propyl, isobutyl, and amyl glycolic nitriles (after fractional distillation), corresponding to the chlor-ether used. These compounds, $R-O-CH_2-CN$, were also transformed into their more immediate derivatives, e.g., $R-O-CH_2-CONH_2$ (etheroxides of glycolamide), $R-O-CH_2-COOH$ (etheroxides of glycolic acid), $R-O-CH_2-COOR'$ (ether-salts of the preceding acids). By this method of formation 80 per cent of the theoretical yield was obtained.

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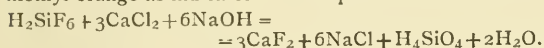
Carbohydrates of Cocoa.—A. D. Maurenbrecher and B. Tollens.—The authors have investigated the individual carbohydrates occurring in cocoa-beans. They first removed the husk and extracted the fat from the beans, and then found in the fat-free powder 5.51 per cent of pentosan. When the powdered beans were extracted with ether and subjected to hydrolysis with sulphuric acid, they found in the products *l*-arabinose, *d*-galactose, *d*-glucose, and probably xylose is also present. The same products are found in the husk. From the fat of the beans, cocoa-butter, the authors succeeded in isolating phytosterin.

Addition Reactions of Dicyandiamide with Inorganic Salts.—Hermann Grossmann and Bernhard Schück.—When aqueous solutions of dicyandiamide and copper sulphate are warmed together on a water-bath, a light blue crystalline precipitate is obtained, while from the light blue filtrate green basic compounds of inconstant composition can be isolated. The formula of the precipitate is $CuSO_4 \cdot 2C_2H_4N_4 \cdot 4H_2O$. The corresponding cadmium compound, $CdSO_4 \cdot 2C_2H_4N_4 \cdot 2H_2O$, crystallises in short colourless prisms. It is much more soluble in water than the copper compound, and is therefore obtained only from concentrated solutions. Pointed glittering needles of $HgCl_2 \cdot C_2H_4N_4$ crystallise from a solution of one molecule of mercuric chloride with two molecules of dicyandiamide.

Atomic Weight of Potassium.—Theodore W. Richards and Arthur Stähler.—For the preparation of the material, pure commercial potassium nitrate was dissolved in a little water, filtered from solid substances, and re-crystallised. The salt was freed from mother-liquor in a porcelain centrifuge, the re-crystallisation repeated in platinum vessels, and the material was then divided into two parts. One was dried *in vacuo*, and the other was re-crystallised six times in platinum vessels. The nitrate was then dissolved in cold water and saturated with pure hydrochloric acid, the platinum vessel in which the operation was performed being surrounded with ice. The potassium chloride

thus obtained was then freed from traces of potassium platinochloride centrifugally. To determine the ratio $\text{KCl}:\text{AgCl}$ the method described by Richards and Wells for the determination of the atomic weight of sodium was adopted. The potassium chloride was weighed in platinum vessels closed with platinum stoppers, all weighings being performed by the substitution method. The silver nitrate used was carefully purified by re-crystallisation, and the precipitation was effected in an Erlenmeyer flask of Jena glass. The potassium chloride solution was introduced into the flask, and small quantities of silver nitrate added in a dark room lighted with a red light only. The filtration was effected in a Neubauer crucible (made by the firm of Heraeus). Special care was taken in correcting for the solubility of silver chloride. To determine the ratio $\text{KCl}:\text{Ag}$, silver was precipitated from re-crystallised silver nitrate by means of ammonium formate, and the metal thus obtained was fused, first in a current of electrolytic hydrogen, and then in a vacuum of 0.1 m.m. in a Heraeus furnace. The fusion took place in a boat of pure calcium oxide. The numbers obtained from the ratio of KCl to AgCl agreed perfectly with those obtained from the ratio of $\text{KCl}:\text{Ag}$. In both cases if $\text{Cl} = 35.473$ and $\text{Ag} = 107.93$, potassium = 39.114 .

Analysis of Hydrofluosilicic Acid.—L. Schucht and W. Möller.—With both methyl-orange and phenolphthalein as indicator the titration of hydrofluosilicic acid with alkali, according to the equation $\text{H}_2\text{SiF}_6 + 2\text{KOH} = \text{K}_2\text{SiF}_6 + 2\text{H}_2\text{O}$, gives slightly inaccurate results, owing to the disturbing effect of the water formed. If, however, excess of neutral calcium chloride solution is added to the hydrofluosilicic acid solution it can be titrated easily in the cold, with methyl-orange as indicator. The equation is:—



Volumetric Determination of Mercury.—E. Rupp.—One to 2 grms. of potassium iodide are added to a solution of a mercuric salt (about 0.2 grm. in 25 to 50 c.c.), the solution is then made alkaline with caustic potash or caustic soda, and a mixture of 2 to 3 c.c. of pure 40 per cent formaldehyde solution and 10 c.c. of water is added, the whole being well shaken. After one-half to one minute acetic acid is added till the mixture smells distinctly of it, and then excess of $\text{N}/10$ iodine (25 c.c.). The finely divided mercury disappears quickly if the solution is shaken thoroughly. When all traces of the metal have disappeared, the excess of iodine is determined with $\text{N}/10$ thiosulphate solution, with or without starch as an indicator. To determine mercurous compounds they must first be converted into the mercuric compound. In the case of the halogen salts this may be effected by means of bromine. For mercurous nitrate and sulphate it is best to acidify with the corresponding acid and add permanganate solution till the red coloration does not disappear. To determine mercury in mercuric cyanide solution, after proceeding as above some sulphuric acid must be added before titrating with thiosulphate.

MEETINGS FOR THE WEEK.

MONDAY, 17th.—Society of Arts, 8. (Cantor Lectures). "Artificial Fertilisers—their Nature and Functions," by A. D. Hall.

TUESDAY, 18th.—Society of Arts, 8. "Basket Making," by T. Okey.

WEDNESDAY, 19th.—Society of Arts, 8. "Modern Developments of Flour Milling," by A. E. Humphries.

Microscopical, 8. Exhibition of Slides from the Collection presented to the Society by Mr. Jas. Hilton.

THURSDAY, 20th.—Chemical, 8.30. "New Laboratory Method for the Preparation of Hydrogen Sulphide," by F. R. I. Wilson. "Reaction of Acids with Methyl-orange," by V. H. Veley. "Contributions to the Study of the Calcium phosphates—(1) The Hydrates of the Calcium-hydrogen Orthophosphates; (2) Action of Ammonia Gas on the Calcium-hydrogen Orthophosphates," by H. Bassett, jun.

MACMILLAN'S LIST.

LIFE AND EXPERIENCES OF
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THE CHEMICAL NEWS.

VOL. XCIV., No. 2456.

NOTE ON FLUORESCENCE, LUMINESCENCE, AND CHEMICAL CONSTITUTION.

By C. S. STANFORD WEBSTER, F.I.C.

IN a recent research of L. Francesconi and G. Bargellini (*Journ. Chem. Soc.*, 1906, ii., 714) by adopting a very delicate method of detecting fluorescence, it has been established that the groups NH_2 , OH , and COOH when attached to the benzene ring increase fluorescence and that NO_2 , Cl , Br , &c., and the substituents acetyl and benzoyl diminish it. It is noteworthy that this increase of fluorescence of a substance in solution when sunlight is the exciting agent runs parallel with the luminescence when the latter is exposed to the rays emitted by a salt of radium; and those groups or substituents which diminish the fluorescence in the first also diminish the luminescence in the second case.

A considerable amount of work on the luminescence peculiar to aromatic compounds has been published by H. Kauffmann (*Journ. Chem. Soc.*, 1906, i., 283), and H. Kauffmann and A. Grombach (*Journ. Chem. Soc.*, 1905, i., 280). Results of a precisely similar character have been obtained by the author in studying the luminescence of aromatic compounds, as, for instance, salicylic acid and derivatives. When these results are tabulated, *i.e.*, in the order of luminescence, it is seen that the order is a certain criterion of constitution.

It is clear therefore that comparative observations of a new compound by means of the luminiscope (*Journ. Soc. Chem. Ind.*, Dec. 31, 1904, p. 1185) affords a means of verifying constitution, and the method is especially useful in cases where a compound is isolated in too minute a quantity for analysis.

FILTER-TUBES FOR COLLECTION OF PRECIPITATES ON ASBESTOS.

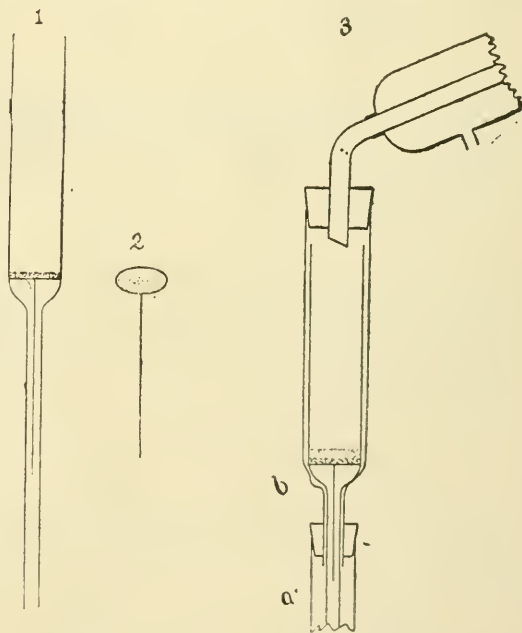
By S. L. PENFIELD and W. M. BRADLEY.

THE tubes described in this article may be employed to advantage in a variety of analytical operations, and as an inexpensive substitute for a Gooch crucible, where a high temperature is not required.

The tubes (Fig. 1) may readily be drawn out from combustion tubing, or made from soft glass if high temperatures are not used. Different lengths and sizes will find a variety of uses, and diameters from 17 to 20 m.m. may be recommended for general use. The most satisfactory support for asbestos is a perforated platinum disc 0.2 m.m. in thickness, to the centre of which a platinum-wire three inches long is soldered (Fig. 2). Where conditions or expense prohibit the use of platinum, a filter-bed of quartz may be substituted with excellent results. A large fragment is used to close the throat of the filter-tube, and on this is placed a layer of powdered quartz about six or eight times as coarse as sea-sand, from which fine material has been carefully removed by screening and washing. In order to deposit a uniform layer of asbestos on the quartz, it is recommended to observe the following precautions:—The bottom of the filter-tube is closed with the finger, and the tube is half filled with water; asbestos suspended in water is then added, when upon removing the finger, it will settle in a smooth layer upon the quartz, and may be firmly fixed by use of a filter-pump. The asbestos and precipitate collected on it dry slowly in the

tubes in an ordinary drying oven, but removal of water may be quickly accomplished by drawing a slow current of air through the tubes, the latter being heated in an air-bath, which may be improvised from a baking-powder can. Such filters may be found useful for collecting many precipitates which need not be subjected to strong ignition, silver chloride, for example, and they are especially recommended for precipitates which are subsequently to be ignited in gases, as will be illustrated by numerous examples. They are admirably adapted for use with an extractor, where either a precipitate collected on the asbestos, or a powder, is to be treated with some solvent, such as either carbon bisulphide or alcohol. The arrangement of a filter-tube in an extractor is suggested by Fig. 3, where *a* is the neck of a flask containing some solvent, the vapours of which pass up between the filter-tube and the outer jacket, and after condensation drop down upon the material collected on the asbestos. At *b* there should be some swelling of the tube to allow a free upward passage of vapours.

In case of a small amount of organic material being present, it could undoubtedly be burned in the tube in oxygen gas and the resulting carbon dioxide and water collected and weighed.



Precipitates collected on the asbestos can be ignited by applying a gentle heat to the tubes while supported in an inclined position, or the following arrangement may be found very serviceable:—A small hole is pierced in the bottom of a porcelain crucible and enlarged by chipping until a hole of the desired diameter is obtained, through which is passed the smaller part of the filter-tube. The crucible not only serves as a support for the tube, but also protects the glass and precipitate from too strong ignition. A ring burner is placed beneath the crucible, and so adjusted that the lower part of the filter-tube passes through the centre of the burner, and may by its lower end be connected to a gas generator. If it is desired to increase the temperature of the upper part of the tube, this may be accomplished by using wire-gauze, so placed as to deflect the heat to that portion.

In order to test the apparatus just described with precipitates requiring ignition in gases, a number of experiments have been carried out with the following results:—

Calcium ignited in CO_2 and weighed as CaCO_3 .

	Precipitated as CaCO_3 .	Precipitated as CaC_2O_4 .
Calcite taken	0.7445	0.7191
CaCO_3 weighed ..	0.7450	0.7195
Error	+0.0005	+0.0004
Error as CaO	0.0003	0.0002

The collection of a considerable portion of calcium oxalate on an asbestos-filter can scarcely be recommended, because the exceedingly fine precipitate clogs the asbestos and makes the filtration tedious.

Copper in re-crystallised copper sulphate was precipitated by means of hydrogen sulphide and ignited in CO_2 .

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ taken = 0.1936.

Cu_2S calculated	0.0617
Cu_2S weighed	0.0618
Error	+0.0001

Zinc in re-crystallised potassium double sulphate $\text{K}_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ was precipitated by hydrogen sulphide in formic acid solution, ignited in CO_2 , and weighed as ZnS .

$\text{K}_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ taken 0.5265.

ZnO calculated	0.0965
ZnO determined	0.0960
Error	-0.0005

Lead in pure galena was precipitated by hydrogen sulphide in acetic acid solution, after decomposing the mineral with nitric acid, and dissolving lead sulphate with ammonium acetate. Lead sulphide was ignited in hydrogen sulphide and weighed.

Galena taken	0.2494
PbS weighed	0.2494
Error	0.0000

Arsenic in sublimed arsenious oxide was precipitated by hydrogen sulphide after dissolving in pure sodium carbonate, and acidifying with hydrochloric acid.

The arsenious sulphide was subjected to the action of carbon bisulphide for the removal of sulphur, using the extractor illustrated by Fig. 3.

As_2O_3 taken 0.1890.

As_2S_3 calculated	0.2350
As_2S_3 weighed	0.2357
Error	+0.0007

Antimony in Japanese stibnite was precipitated by hydrogen sulphide after dissolving the mineral in hydrochloric acid. The Sb_2S_3 was ignited in CO_2 gas.

Stibnite taken	0.1385
Sb_2S_3 weighed	0.1384
Error	-0.0001

Bismuth in pure Bi_2O_3 was precipitated by hydrogen sulphide after dissolving the oxide in the least possible amount of dilute nitric acid, and diluting largely before precipitation.

Bi_2S_3 was ignited in CO_2 and weighed.

Bi_2O_3 taken	0.3047
Bi_2O_3 determined	0.3046
Error	-0.0001

Thanks are here expressed to Dr. W. E. Ford, who kindly furnished the results of the last two determinations.

Filter-tubes such as here described have been in use for many years in our laboratory, and have frequently been employed in the estimation of potassium as platonic chloride; on subsequent ignition in hydrogen gas the salt may be decomposed, the alkali chloride extracted with water, and tested spectroscopically for caesium and rubidium.—*American Journal of Science*, [4], xxi., No. 126.

THE USE OF THE ROTATING CATHODE FOR THE ESTIMATION OF CADMIUM TAKEN AS THE CHLORIDE.

By CHARLES P. FLORA.

In a previous paper the author has described the use of the rotating cathode for the estimation of cadmium taken as the sulphate (*Am. Journ. Sci.*, 1905, xx., 268; *CHEMICAL NEWS*, xciv., pp. 274, 283). In the present paper a similar study has been made of the behaviour of cadmium when taken in the form of the chloride. Some differences are to be expected, since it has been established with some certainty that cadmium chloride, when subjected to electrolysis, forms not only positive cadmium ions and negative chlorine ions, but also complex cadmium-chlorine negative ions; and, in addition, the chlorine, when set free, does not re-combine with the water, to set free oxygen, but exists in the solution in its free state. That there are some very important differences a few qualitative experiments showed, so that the study of the estimation of cadmium when taken in the form of this salt was now undertaken.

A solution was made up to a convenient strength, and the standard determined by the mean of several closely agreeing determinations by the carbonate method, which the author had carefully tested and found to be perfectly reliable. This showed 0.1589 gm. of cadmium in 30 c.c. of the solution, or 0.0052966 gm. per c.c.

I. In Solutions containing Sulphuric Acid.

The procedure with cadmium chloride was the same as with the cadmium sulphate, and the results were very satisfactory. But emphasis is to be laid upon the dilution in this case especially, for it was found that from the more dilute solution it is almost impossible to drive the last traces of cadmium. A dilution of 45 c.c. was found to give the most satisfactory results. To this solution ten drops of sulphuric acid of 1:4 dilution were added before electrolysis. The results obtained under these conditions are given in Table I.

II. In Solutions containing Acetates.

The acetate method has proved one of the most satisfactory for the estimation of cadmium sulphate, but strangely enough, it was found to be absolutely unfitted for the estimation of cadmium when taken as the chloride. The deposited metal was always spongy, often non-adherent and unfitted for quantitative work. The sponginess was less marked when no potassium sulphate was present, but the metal was still poorly adherent and unweighable. The modifications tried are given for the sake of comparison in Table II. The current potential throughout was 7.8 volts, while the dilution, excepting in experiment No. 4, was 45 c.c. In No. 4 a dilution of 65 c.c. was tried, but it offered no apparent advantage.

III. In Solutions containing Cyanides.

The use of a cyanide solution gave results with the chloride of cadmium as satisfactory as were given when the sulphate of cadmium was taken. As in that case, care must be taken to avoid foaming of the solution. The best dilution seemed to be 65 c.c. The time required is a trifle longer than in the estimation of cadmium sulphate by this method. The results obtained are given in Table III.

In experiment No. 2 there was much foaming, and a trace of cadmium remained in solution, the deposition being much retarded.

IV. In Solutions containing Pyrophosphates.

The different modifications of the pyrophosphate method gave results which were quite satisfactory, and in every respect comparable with the results obtained with this electrolyte in the estimation of cadmium sulphate. As was the case with that salt, the use of ammonium hydroxide to

TABLE I.

No.	Cd. Grm.	Current = Ampères.	N.D.100. Ampères.	E.M.F. Volts.	Time. Minutes.	Cd found. Grm.	Error. Grm.
1.	0.1059	1.0—1.5	3.0—4.5	6.5—7.8	25	0.1054	-0.0005
2.	0.1059	2.0—3.0	6.0—9.0	7.8	15	0.1058	-0.0001

TABLE II.

No	Cd. Grm.	NaOC ₂ H ₃ O. Grm.	K ₂ SO ₄ . Grm.	Current = Ampères.	N.D.100. Ampères.	Time. Minutes.	Notes.
1.	0.1324	1.5	0.5	1.5	4.5	13	Very spongy.
2.	0.1324	1.5	None	1.0	3.0	8	0.1314 grm. found.
3.	0.1059	1.0	None	0.75	2.25	20	Non-adherent.
4.	0.1059	1.5	0.5	1.5	4.5	—	Spongy, non-adherent.
5.	0.1059	1.5	None	1.0	3.0	—	2 c.c. formalin added; spongy.
6.	0.1059	1.5	None	0.75	2.25	—	Non-adherent, crystalline.
7.	0.1059	0.5	0.5	1.0	3.0	—	" "

TABLE III.

No:	Cd. Grm.	KCN. Grms.	NaOH. Grm.	Current = Ampères.	N.D.100. Ampères.	E.M.F. Volts.	Time. Minutes.	Cd found. Grm.	Error. Grm.
1.	0.1324	1.5	1.0	4	12	7.8	35	0.1322	-0.0002
2.	0.1324	1.5	1.0	4	12	7.8	40	0.1317	-0.0007

TABLE IV.

No.	Cd. Grm.	Solvent.	Current = Ampères.	N.D.100. Ampères.	Time. Minutes.	Cd found. Grm.	Error. Grm.
1.	0.1324	1 c.c. concentrated NH ₄ OH	0.5	1.5	15	0.1327	+0.0003
2.	0.1324	12 drops H ₂ SO ₄ (1.4)	0.75	2.25	35	0.1328	+0.0004
3.	0.1324	15 drops H ₃ PO ₄ (sp. gr. 1.7)	0.75—1.0	2.25—3.0	30	0.1331	+0.0007
4.	0.1324	15 drops HCl (1:4)	0.7—0.5	2.1—1.5	45	0.1319	-0.0005

TABLE V.

No.	Cd. Grm.	HNa ₂ PO ₄ . Grm.	H ₃ PO ₄ (sp. gr. 1.7). c.c.	Current = Ampères.	N.D.100. Ampères.	E.M.F. Volts.	Time. Minutes.	Cd found. Grm.	Error. Grm.
1.	0.1059	0.25	5 c.c.	2.0—3.0	6.0—9.0	7.8	15	0.1082	+0.0023
2.	0.1324	0.25	2.5 c.c.	2.0—3.0	6.0—9.0	7.8	13	0.1344	+0.0020
3.	0.1324	0.20	10 drops	1.0	3.0	7.8	15	0.1330	+0.0006
4.	0.1324	0.20	6 drops	0.25	0.75	7.8	35	0.1310	-0.0014

TABLE VI.

No.	Cd. Grm.	Urea. Grm.	Current = Ampères.	N.D.100. Ampères.	E.M.F. Volts.	Time. Minutes.	Total vol. C.c.	Cd found. Grm.	Error. Grm.	Notes.
Series A.—Urea.										
1.	0.1324	3	1.0	3.0	12	20	60	0.1312	-0.0012	Spongy; not all out.
2.	0.1324	2	1.0	3.0	12	30	60	0.1336	+0.0012	" "
3.	0.1324	3	1.0	3.0	7.8	15	55	0.1342	+0.0018	Very spongy; all out.
4.	0.1324	2	0.25	0.75	7.8	25	60	0.1324	0.0000	All out.
5.	0.1324	2	0.5	1.5	12	20	60	0.1333	+0.0009	Slightly spongy; all out.
6.	0.1324	1	1.0	3.0	12	20	60	0.1370	+0.0046	Very spongy.
7.	0.1324	1.5	0.25—0.5	0.75—1.5	7.8	30	60	0.1328	+0.0004	Good.
8.	0.1324	1.5	0.25—0.5	0.75—1.5	7.8	30	60	0.1329	+0.0005	Fair.
Series B.—Formaldehyde (Formalin).										
Formaldehyde.										
1.	0.1324	3.0 c.c.	0.25—1.5	0.75—4.5	7.8	20	45	0.1333	+0.0009	Fair.
2.	0.1324	2.0 "	0.50—2.0	1.50—6.0	11.8	15	45	0.1330	+0.0006	Slightly spongy.
3.	0.1324	1.5 "	0.75	2.25	7.8	30	60	0.1324	0.0000	Compact.
4.	0.1324	1.5 "	1.0	3.0	7.8	35	60	0.1325	+0.0001	Compact.
Series C.—Acetaldehyde (95 per cent).										
Aldehyde (95 %).										
1.	0.1324	2.0 c.c.	0.2—0.7	0.6—2.1	7.8	30	60	0.1311	-0.0013	Not all out; slightly spongy.
2.	0.1324	1.5 "	0.5—0.75	0.6—2.25	7.8	30	60	0.1346	+0.0022	Spongy.
3.	0.1324	0.5 "	0.2—1.0	0.6—3.0	7.8	65	60	0.1307	-0.0017	Spongy; not all out.
4.	0.1324	1.0 "	0.1—0.75	0.3—2.25	8.0	35	60	0.1328	+0.0004	Fair.

dissolve the precipitate gave the most satisfactory results; while after that, sulphuric acid seemed to be the most suitable solvent. The deposits obtained from solutions to which were added free phosphoric acid showed a slight tendency toward sponginess. When hydrochloric acid was added, the deposits were good but deposition was slow. The total volume in each case was 45 c.c.; the amount of sodium pyrophosphate used was 9.5 grms.; while the current potential was 7.8 volts. The results obtained are given in Table IV.

V. In Solutions containing Phosphates.

With cadmium chloride, hydrogen disodic phosphate must be used with even more care than with cadmium sulphate, if deposits which are even slightly satisfactory are to be obtained; and even when used with caution, the tendency to form spongy deposits is so persistent that this method is not to be recommended where other methods are available. Table V. gives the solutions tried, the concentration being 45 c.c. throughout.

Nos. 1 and 2 gave spongy deposits; No. 4 showed no colour upon testing the solution at the end of the operation with hydrogen sulphide, but this test does not seem to be very sensitive in this solution. No. 3 seems to represent the best conditions.

VI. In Solutions containing Oxalates.

Several qualitative tests, using conditions identical with those giving the least unsatisfactory deposits with cadmium sulphate, were tried upon the cadmium chloride, with like unsatisfactory results, so that the work upon the oxalate method was not pursued further.

VII. In Solutions containing Urea, &c.

A few qualitative tests seemed to indicate that solutions containing urea, formaldehyde, or acetaldehyde would furnish very satisfactory media for the estimation of cadmium, taken in the form of the chloride, but further experimentation proved these appearances to be deceptive. Under these conditions, the cadmium is deposited much more quickly from a solution of its chloride than of the sulphate, and the deposit in the earlier part of the precipitation appears to be very satisfactory. But the chlorine set free apparently has some action upon the organic compound present to produce substances detrimental to the process. With care, however, satisfactory results may be obtained, as may be seen from a study of Table VI.

The amount of urea present, therefore, should be between 1.5 grm. and 2 grms., and the current potential should not exceed 8 volts, instead of the 12 volts permissible when cadmium sulphate was used. The test with hydrogen sulphide does not seem to be very delicate in this solution, so that at least thirty minutes should be allowed for each determination. Some writers recommend the testing of the end-point in similar cases by raising the level of the liquid upon the cathode, but this was not proved of much value in this work, as the amount of metal deposited upon the fresh cathode surface from the solutions near the end of the process is imperceptible.

A solution to which formaldehyde was added gave the results stated in Series B.

It will be seen from these results that it is better to use a somewhat smaller quantity of formaldehyde than was used with the cadmium sulphate; the current potential should not exceed 8 volts, while the solution should be rather dilute (60 c.c.).

These cautions are of even greater importance when acetaldehyde is used, if satisfactory results are to be obtained, as shown in Series C.

VIII. In Solutions containing Formates and Tartrates.

Like cadmium sulphate, so also cadmium chloride gave negative results when solutions containing in addition potassium formate in the presence of formic acid were subjected to electrolysis. Moreover, when no formate was added, but formic acid alone, the results were still unsatis-

factory. To solutions containing 0.1324 grm. of cadmium in the form of the chloride was added 1.5 c.c. of formic acid, the whole diluted to 50 c.c., and electrolysis conducted under potentials of 7.5 and 11.8 volts. In each case the precipitate was spongy and non-adherent, while the solution persistently held traces of cadmium, even after subjecting to the current nearly two hours.

Solutions containing tartaric acid behaved in a similar manner. In the presence of 3 grms. of tartaric acid, under current tensions of 8 and 12 volts, the precipitated metal peeled from the cathode during revolution, the deposit was spongy, and deposition seemed to be complete at no point of the operation.—*American Journal of Science*, xx., p. 392.

ADDITIONAL NOTES UPON THE ESTIMATION OF CADMIUM BY MEANS OF THE ROTATING CATHODE, AND SUMMARY.

By CHARLES P. FLORA.

I. The Behaviour of Cadmium Nitrate.

SINCE cadmium is not readily precipitated by the electric current from solutions containing even small amounts of free nitric acid, it was to be expected that cadmium nitrate would prove to be little fitted for estimation by electrolysis, since the action of the current would produce nitric acid. This, in general, was the result of my experiments upon the estimation of cadmium in the form of the nitrate upon the rotating cathode. The deposits obtained from solutions containing sulphuric acid, the phosphates, pyrophosphates, urea, or formaldehyde, were satisfactory, but the time necessary for complete deposition is so prolonged that these solutions are comparatively valueless for the estimation of cadmium taken as the nitrate, since it would be easier and more trustworthy to transform the salt to the sulphate by evaporation with sulphuric acid before electrolysis. With solutions containing acetic acid the metal was not precipitated except in a narrow ring at the surface of the liquid. The behaviour of solutions containing formic acid, tartaric acid, acetaldehyde, and formaldehyde was similar, but less pronounced. The only solution from which I was able to obtain satisfactory results in the estimation of cadmium nitrate was a solution containing potassium cyanide. This solution was prepared by adding to the solution of cadmium nitrate, which had been standardised by the precipitation and ignition of the carbonate, the desired amount of sodium hydroxide, and then re-dissolving the precipitated hydroxide in an excess of potassium cyanide. The time needed for complete deposition is somewhat longer than that required where the chloride and sulphate of cadmium were taken, but the deposit was bright and very satisfactory. Care must be used to avoid the use of too large an amount of potassium cyanide. The following table shows the results obtained:—

	1.	2.	3.
Cadmium taken (grm.) ..	0.0920	0.0920	0.1073
Cadmium found (grm.) ..	0.0933	0.0924	0.1072
Error (grm.) ..	+0.0013	+0.0004	-0.0001
KCN (grm.) ..	1.5	1.0	0.7
NaOH (grm.) ..	0.5	0.5	0.5
Current (ampère) ..	4.0	3.0	2.5
N.D. ₁₀₀ (ampère) ..	12.0	9.0	7.5
E.M.F. (volts) ..	7.8	7.6	7.7
Time (minutes) ..	45	35	50
Total volume (c.c.) ..	60	60	60

II. Behaviour of Solutions containing Free Nitric Acid.

If free nitric acid be added to a solution containing a salt of cadmium, the precipitation of the cadmium by the electric current will be retarded, and even prevented altogether if the nitric acid be present in sufficient amount. Upon this behaviour have been based methods for the

separation of copper, bismuth, and mercury from cadmium (Edgar F. Smith, *Am. Chem. Journ.*, 1880, ii., 42; Smith and Mayer, *Journ. Am. Chem. Soc.*, 1893, lxiv., [ii.], 496); Kammerer, *Journ. Am. Chem. Soc.*, 1903, xxv., 94; Rüdorff, *Zeit. Angew. Chem.*, 1894, 388). Tests were made by me to determine the amount of free nitric acid necessary to prevent deposition of the cadmium, and it was found that 2 c.c. of nitric acid of 1 : 4 dilution in 50 c.c. of solution (approximately 1 per cent of free acid) will absolutely prevent the precipitation of the cadmium upon the cathode (current, 3 ampères; E.M.F., 7.5 volts). If less nitric acid was used, traces of cadmium were deposited upon the cathode.

Summary of Results obtained in the Estimation of Cadmium by means of the Rotating Cathode.

The results of the work described in this and the previous papers upon the estimation of cadmium by means of the rotating cathode may be briefly summarised as follows:—Under the conditions used, cadmium taken in the form of the sulphate may be very accurately and satisfactorily estimated by deposition from solutions containing sulphuric acid, sodium acetate, and acetic acid, or potassium cyanide; but little less satisfactorily from solutions containing urea, formaldehyde, or acetaldehyde; and also with proper precautions, from solutions containing pyrophosphates, phosphates, tartaric acid, or formic acid. From solutions containing oxalates or oxalic acid, ammonium tartrate, or potassium formate, however, I was unable to obtain satisfactory deposits. When taken as the chloride, cadmium does not permit such a wide range of conditions. Nevertheless, from solutions of the chloride containing sulphuric acid or potassium cyanide, or the pyrophosphates, the metal is deposited in a form comparable with that obtained when cadmium sulphate is taken. Solutions of the chloride of cadmium to which is added hydrogen disodic phosphate gave less desirable results; while solutions containing urea, formaldehyde, or acetaldehyde gave deposits free from sponginess only after careful regulation of the conditions. In addition to the solutions containing the oxalates, oxalic acid, the formates, and the tartrates, negative results were given in the case of the chloride by solutions containing the acetates, formic acid, and tartaric acid. The nitrate of cadmium is ill-fitted for electrolytic estimation, the cyanide solution being the only one from which satisfactory results were obtained. From solutions containing 1 per cent or more of free nitric acid, the cadmium is not deposited by the current.—*American Journal of Science*, xx., p. 453.

COLOUR REACTIONS OF CERTAIN ORGANIC COMPOUNDS.

By Prof. E. PINERUA ALVAREZ.

By means of the new general reagent of the polyphenols and their isomers, the hydrate of sodium dioxide ($\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$) prepared from sodium dioxide ($\text{Na}_2\text{O}_2 = 2\text{NaO}$), pure ethyl alcohol ($D = 0.797$), and cold water, we may identify the compounds of which we shall speak, by using a little porcelain capsule in which from 5 to 10 centigrams. of the body is placed, with 2 or 3 decigrams. of dioxide and 5 c.c. alcohol, and, after allowing the bodies to react for four to six minutes, adding 15 c.c. distilled water.

The colourations produced are the following:—

Emodine.—Intense pink colour, which becomes yellow with several drops of acetic acid.

Chrysorobine.—Wine colour, which persists when water is added. With acetic acid it also becomes yellow.

Dioxyanthraquinone-1.2.—Beautiful violet-blue colour, which persists on adding water. On immersing the

capsule in the liquid and blowing, the edges of contact become red. With acids, the liquid acquires an intense yellow colour.

Alizarin.—Violet colouration, becoming orange with acids.

Trioxanthraquinone-1.2.4.—Intense red-violet, changing to cherry-red on addition of water.

Chrysophanic Acid.—Cherry-red colour which with water becomes brighter.

Rosolic Acid.—Intense purple colour, which persists with water.

Purpurine-alizarin.—Intense and very beautiful pink colour, which persists on adding water.

Anthrogallol.—Dark blue colour, almost black, unchanging.

Dioxyquinone.—Brown-yellow colour, changing to red with water.

Ellagic acid.—Brown-black colour, becoming yellow with addition of water.

ADOPTION OF A SYSTEM OF NOMENCLATURE FOR DESIGNATION OF THE CONDENSED INORGANIC COMPOUNDS.*

By Prof. E. PINERUA ALVAREZ.

I HAVE the honour of proposing to the Congress the adoption of a system of nomenclature for distinguishing clearly and simply numerous and important condensed inorganic compounds, which have no name or are improperly named.

We frequently find that many molecules of the same acid unite and condense into a single one, originating a series of other acids of different properties (polymers), to which is given a distinct name, formed by placing before the fundamental, simple or not condensed, the prefixes *mono*, *di*, *tri*, *tetra*, *penta*, *hexa*, &c.

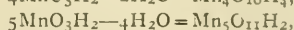
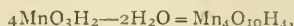
We say, for example, *dimetaphosphoric*, *trimetaphosphoric*, *tetrametaphosphoric*, *hexametaphosphoric acid*, names expressing that these bodies are formed by *two*, *three*, *four*, or *six* molecules condensed into one, of the acid HPO_3 , *metaphosphoric*.

Whilst keeping this method of nomenclature for those bodies only which result from *simple condensation*, our proposal will serve to designate compounds of complex function, both anhydrides and acids, *resulting from the condensation of an acid with simultaneous elimination of one or several molecules of water*. It could also be applied to the corresponding metallic derivatives.

The system consists simply in adding to the specific name of the condensed acid a number expressing the molecules of water eliminated.

Thus, for example, the compound $\text{Mn}_2\text{O}_5\text{H}_2$, resulting from the condensation of 2 mols. of manganous acid with elimination of one of water, $2\text{MnO}_3\text{H}_2 - \text{H}_2\text{O} = \text{Mn}_2\text{O}_5\text{H}_2$, and has actually no name, should be called *dimanganous acid-1*, and its metallic derivative, $\text{Mn}_2\text{O}_5\text{K}_2$, *potassium dimanganite 1*.

The compounds $\text{Mn}_4\text{O}_{10}\text{H}_3\text{K}$ and $\text{Mn}_5\text{O}_{11}\text{K}_2$, derived respectively from the acids *tetramanganous-2* and *pentamanganous-4*, according to the following equations:—



will be called *monopotassium tetramanganite-2* and *potassium pentamanganite-4*.

By adopting this system, ordinary ammonium molybdate, $\text{Mo}_7\text{O}_{24}(\text{NH}_4)_6$, derived from the acid heptamolybdic-4, $7\text{MoO}_4\text{H}_2 - 4\text{H}_2\text{O} = \text{Mo}_7\text{O}_{24}\text{H}_6$, will be called ammonium heptamolybdate-4.

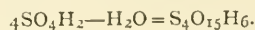
* Note presented at the Sixth International Congress of Applied Chemistry, held at Rome, 1906.

* Note presented at the Sixth International Congress of Applied Chemistry, held at Rome, 1906.

Borax derived from the acid tetraboric-5 will receive the name sodium tetraborate-5, $4\text{BO}_3\text{H}_3-5\text{H}_2\text{O}=\text{B}_4\text{O}_7\text{H}_2$.

By the same reasoning, the compound derived from the acid $\text{S}_2\text{O}_5\text{H}_2$, disulphurous-1, will be called *disulphites-1*, and the pyrosulphates, pyrophosphates, pyroarsenates, pyrantimonates, &c., will be called *disulphates*, *diphosphates*, *diarsenates*, *diantimonates-1*.

The compound $\text{S}_4\text{O}_{13}\text{H}_2$, discovered by Weber, which has no name, will be, according to this system, the acid *tetrasulphuric-3*, $4\text{SO}_4\text{H}_2-3\text{H}_2\text{O}=\text{S}_4\text{O}_{13}\text{H}_2$, and $\text{S}_4\text{O}_{15}\text{H}_6$ will be the acid *tetrasulphuric-1*,—



The same system will apply to the numerous polyiodic, polyperiodic, polysulphurous, polyphosphorous, polyphosphoric, polysilicic, polystannic, polyniobic, polytantalic, polymolybdic, polytungstic, &c., compounds.

I would ask the Congress for an opinion on this proposition.

NOTE ON THE ESTIMATION OF NIOBIUM AND TANTALUM IN THE PRESENCE OF TITANIUM.

By C. H. WARREN.

THE obtaining of a strong reaction for niobium in the mineral described in a previous paper and the failure to obtain more than a fraction of a per cent of niobium by means of the acid potassium sulphate fusion and leaching in cold water, naturally led to an examination of the methods for estimating these elements quantitatively in the presence of each other.

So far as the writer can ascertain, the most common method followed is that involving a fusion with bisulphate of potash followed by leaching with cold water, these operations being repeated until all the titanium has passed into solution, while the niobic and tantallic oxides remain behind. Dr. A. A. Noyes states that when treated in this manner fairly large quantities of niobium and tantalum pass into solution with titanium when much of the latter is present ("System of Qualitative Analysis," *Technology Quarterly*, 1904, xvii., No. 3, p. 218: *CHEMICAL NEWS*, xciii., p. 134 *et seq.*). With this statement in mind a few experiments were made to gain some further idea of the magnitude of the error involved in the method.

Pure TiO_2 was prepared from selected crystals of rutile by the usual chemical methods. Nb_2O_5 and Ta_2O_5 were prepared from the columbite of Branchville, Conn., after the method described by Osborne (*Am. Journ. Sci.*, 1885, [3], xxx., 330), except that the precipitated oxides were digested for some time with ammonium sulphide to insure the removal of any tungsten or tin which might be present. The final products were subjected to the most careful qualitative examination, and no impurity other than a trace of iron could be detected.

The attempts at separating these oxides, quantitatively, when mixed together were very unsatisfactory, and although few in number seem to thoroughly confirm Dr. Noyes's statement. Indeed, considerable quantities of niobium may be made to pass into solution with the titanium, as the figures given below show. In the first three experiments, the fusion and leachings were thrice repeated. In each case the fusion was mashed to a powder under cold water in an agate mortar, and allowed to stand with from 250 to 300 c.c. of water for twenty-four hours. The titanium was precipitated from the combined filtrates with ammonium hydroxide, filtered, washed free from sulphates, and ignited to a constant weight. The residues from the first two leachings gave a strong reaction for titanium with hydrogen peroxide, and a small amount of titanium always remained in the last residue.

No.	$\text{Nb}_2\text{O}_5-\text{Ta}_2\text{O}_5$ (about 3:1) taken.	TiO_2 .	Weight of oxides extracted.	Excess.
1.	0.2500	0.2359	0.3046	0.0687
2.	0.2103	0.2039	0.2580	0.0541
3.	0.3031	0.2698	0.2883 (b)	0.0185
4.	0.0178 (a)	0.3605	0.0010 (c)	—

(Weights in grm.)

(a) Nb_2O_5 only.

(b) Still gave a strong reaction for titanium.

(c) Niobium undissolved.

From No. 4 it would appear that as much as 5 per cent of niobium may pass into solution with an excess of titanium, and thus be practically lost in the course of analysis. Although further study of the most favourable conditions of fusion and solution might be of interest in themselves, the method appears to offer little chance of being modified so as to give more than roughly approximate results.

The method proposed by T. B. Osborne was next examined ("The Quantitative Estimation of Niobium," *Am. Journ. Sci.*, 1885, [3], xxx., pp. 328—337). This depends on the titration of a solution containing the titanium and niobium in the lower state of oxidation with potassium permanganate, thus oxidising these elements to the higher oxides, and the subsequent estimation of titanium colorimetrically, while any tantalum, which is not reduced to the lower oxide, present in the original sample, is found by difference. The method of procedure is briefly this:—The mixture of the three acids, tantallic, niobic, and titanic, is dissolved in hydrofluoric acid, and the excess of acid expelled on the water-bath. The fluorides thus obtained are dissolved in concentrated hydrochloric acid, washed with the same acid into a 100 c.c. flask (total volume about 50 c.c.), and reduced for three-quarters of an hour with amalgamated zinc and a piece of platinum-foil in an atmosphere of carbon dioxide at a temperature of 80°C . The reduced solution is cooled thoroughly, diluted with freshly boiled cold water to about 350 c.c., and titrated with permanganate. To this solution ammonia is added in slight excess, the precipitate formed, just dissolved in sulphuric acid, and the volume made up to exactly 500 c.c. The titanium is then estimated colorimetrically, with hydrogen peroxide in 50 c.c. portions of this solution.

For any except small amounts of titanium the colorimetric method is open to the serious objection that any error in estimating the amount of titanium in the aliquot portion (and that error can hardly fail to be considerable where a large amount of titanium is present) is multiplied by ten in estimating the total amount present. Mr. Osborne gives the result of only a single application of the method. The figures are as follows:—

	Nb_2O_5 .	Ta_2O_5 .	TiO_2 .
Taken ..	0.3357	0.2246	0.0687
Found ..	0.3314	0.2289	0.0667

(Weights in grm.)

The agreement here is quite satisfactory, but as the relative amount of titanic oxide is small, and as the writer had never had any experience with the method, it was decided to make a trial of the method before using it in an analysis. In Experiments 1 to 4 of those given below Mr. Osborne's directions were followed closely. In Nos. 5 and 6 the time of reduction was increased, and in No. 6 the volume of acid was doubled. One other experiment was tried, and the temperature raised to nearly 100°C ; but as a separation of the metallic acids took place this one is not included. The results obtained by reduction and titration are as shown in Table (see next column).

The large size and irregularity of the resulting errors led the writer to abandon further work on the method with the conclusion that it is wholly unsatisfactory as it stands. One source of error in the method is possibly the loss of some volatile, metallic fluoride during the removal of the

Time of reduction: Nos. 1—4, three-quarters of an hour; Nos. 5 and 6, one hour.
Temperature: 80° C.
Volume: Nos. 1—5, 50 c.c.; No. 6, 100 c.c.
Weights in grms.

No.	Nb ₂ O ₅ .	Ta ₂ O ₅ .	TiO ₂ .	KMnO ₄ required.	KMnO ₄ used.	Differences.
1.	0.2163	0.1649	0.2453	0.1988	0.1450	-0.0540
2.	0.2034	0.1062	0.2083	0.1783	0.1551	-0.0232
3.	0.2067	0.1090	0.0708	0.1254	0.1138	-0.0116
4.	0.2283	0.1054	0.2079	0.1899	0.1630	-0.0269
5.	0.1889	—	0.1933	0.1565	0.1317	-0.0248
6.	0.2140	—	0.2033	0.1814	0.1620	-0.0183

hydrofluoric acid on the water-bath. The addition of sulphuric acid with the hydrochloric in order to prevent such volatilisation is inadvisable, since, as Mr. Osborne states, the reduction of the niobium is then far from constant, and it may be added, the tendency of the metallic acids to precipitate during reduction would be greater.

There appears to be, so far as the writer can discover, no method by which more than a rough approximation toward a quantitative separation of these elements can be effected, notwithstanding the numerous analyses purporting to have accomplished a separation of sufficient accuracy to warrant considerable speculation as to the chemical constitution of the group of minerals containing these elements. The problem of their separation is an extremely interesting one mineralogically as well as chemically, since the constitution of so many highly interesting minerals depend on its successful solution. The increasing use of tantalum in lamps and perhaps in other ways, and its common occurrence with niobium and titanium, make a satisfactory quantitative separation of these elements highly desirable, and it is to be hoped that it may soon be realised.—*American Journal of Science*, [4], xxii., No. 132.

VOLUMETRIC METHOD FOR THE ESTIMATION OF CARBON IN IRON AND STEEL WITH THE USE OF BARIUM HYDROXIDE.*

By JAMES A. AUPPERLE.

THE method which I am about to describe has been found to compare very favourably with results obtained by gravimetric methods, with the advantage of being more rapid. It is based upon the following data:—

First.—Barium hydroxide can be titrated with acids in the presence of barium carbonate (which is neutral or faintly alkaline to phenolphthalein), and no carbonic acid will be lost.

Second.—Carbonic acid is indicated by phenolphthalein, and when any barium carbonate is dissolved by standard acid during titration, the fact will be shown by the change in colour.

Third.—Barium hydroxide can be titrated with acids without filtering off the barium carbonate, providing the acid is run into the mixture by a prolongation of capillary tube attached to the burette and extending well into the solution that is being titrated.

The reason for using the capillary tube is that if any carbonic acid be liberated in the lower portion of the beaker, it would be reabsorbed by the upper portion containing barium hydroxide.

Hydrochloric acid has been found to give the best results, and an acid a trifle less than N/5 is used. This is prepared by mixing 15 c.c. of acid (1.20) and 1000 c.c. of water. One c.c. will approximately equal 0.001 grm. carbon.

The barium hydroxide solution is prepared from 31.5

grms. of Merck's crystallised salt, Ba(OH)₂·8H₂O, dissolved in 1000 c.c. of boiled water. When both acid and alkali are at room temperature, and without waiting for the suspended barium carbonate to settle completely, a measured portion is titrated with acid, and the remaining barium hydroxide is then diluted with water, so that 1 c.c. = 1 c.c. of acid. The barium hydroxide is then allowed to stand until clear, and again titrated with acid.

The phenolphthalein solution is 1 to 30 of alcohol, and as it usually contains acid, it is rendered pink with dilute caustic soda or potash. Three drops of phenolphthalein are used for each titration.

When sulphuric or oxalic acid is used for titrating, the barium sulphate or oxalate formed in addition to the barium carbonate present, renders them less desirable than hydrochloric acid, which forms no precipitate.

In using this method in connection with burning steel filings in a current of oxygen, an accurate determination of carbon can be made in twenty minutes, which includes the time consumed in filing the steel.

I have found that filings carefully taken check well in carbon, as found in borings secured in the usual manner, with the advantage that an ignition can be made at a lower temperature and in less time.

The following table will show how the time is distributed in making a direct combustion:—

	Minutes.
Filing the sample	4
Weighing sample and placing dish in Aupperle combustion crucible	2
Measuring barium hydroxide, attaching Meyer tube to combustion apparatus, starting oxygen, and lighting gas	3
Ignition of borings	8
Emptying, washing bulb, and titrating	3
	20

In filing the sample, a large file which has been previously cleaned with a stiff brush is used. The filings are weighed and placed in a platinum dish that fits the Aupperle crucible. This dish contains a one-eighth inch layer of 120 mesh emery, which is heavier than the precipitated alumina ordinarily used and is not so easily projected out of the dish.

The platinum dish is covered with a disk of platinum foil perforated in two semi-circles which form wings, one bent into and the other out of the dish. The wings are bent at angles of 45°, which prevent anything being projected out of the dish.

I have found that with two ounces of gas pressure and gas averaging 700 B.T.U. per cubic foot the crucible becomes white hot, and steel filings are completely oxidised in eight minutes. A Bunsen vertical blast-lamp gives good satisfaction.

At least twenty pounds of air pressure should be used. A single cylinder compressor making 150 revolutions per minute gives enough air for two lamps. By simply closing the valve through which the air enters the pump, a five-pound vacuum can be maintained and used for suction filtering.

Mr. Philo Kemery, of the Crescent Steel Works, Pittsburg, devised the spiral duct tube of the Aupperle crucible which I have adopted and found very satisfactory. The present form of the crucible has one coil of the duct tube around the crucible and joined to the side instead of the bottom. This permits more heat to be concentrated on the bottom of the crucible, and the duct tube becomes hot enough to oxidise all carbon to carbon dioxide.

The standard barium hydroxide and standard acid are contained in bottles holding twelve litres, each bottle being supplied with compressed air in order to facilitate rapid measuring.

The air that enters the barium hydroxide bottle is passed through a solution of caustic potash.

The capillary tube attached to the burette stop-cock is about five inches long.

* Read before the Indiana Section of the American Chemical Society at Lafayette, Ind., May 12, 1906. From the *Journal of the American Chemical Society*, xxviii., No. 7.

For carbon determinations in steel 75 c.c. of barium hydroxide are used, but for iron 150 c.c. contained in two Meyer tubes should be used, each containing 75 c.c. The second tube will only show a precipitate of barium carbonate when a very rapid current of oxygen gas is used, or when the sample is extremely high in carbon. Iron borings should be ignited for twelve to fifteen minutes, and the oxide of iron remaining in the dish should be fused into one globule. The original shape of the borings should then have entirely disappeared.

The barium hydroxide and carbonate are poured into a beaker, and the Meyer tube rinsed three times with boiled distilled water. Three drops of phenolphthalein indicator are added and standard acid run in very rapidly until the red colour disappears and the white barium carbonate is seen. The beaker is then removed and placed under a burette containing standard barium hydroxide, which is added slowly, and until the original red colour returns. The number of cubic centimetres barium hydroxide used in titrating back is subtracted from the acid burette reading. Only about 1 c.c. is usually required.

In experimenting to find how much carbon dioxide would be lost by adding sufficient standard acid to dissolve all the barium carbonate, and immediately titrating back with barium hydroxide, 75 c.c. of acid were added to the mixture of barium hydroxide and carbonate from a 0.90 per cent carbon steel, and on titrating back to original pink 0.88 per cent was found, thus showing practically no loss of carbon dioxide even when all barium carbonate is dissolved.

The acid is standardised with steel or iron of known carbon content. For steel the theoretical value may be used, 1 c.c. N/5 acid = 0.0012 gm. carbon. The following table shows how well the method checks with the gravimetric methods:—

Weighing as BaCO₃.

	Gravimetric. 3-Grm. samples.	Volumetric. 3-Grm. samples.
Steel standard . .	0.090	0.090
"	0.115	0.113
"	0.380	0.393
"	0.643	0.627
"	0.735	0.725
	1-Grm. samples.	1-Grm. samples.
"	0.890	0.890
"	1.130	1.150
"	1.350	1.330
Iron	2.89	2.93
"	3.30	3.35
International standard	3.25	3.31
"	3.67	3.65
Iron	3.76	3.72
"	4.30	4.32

The following results are reported by Mr. J. C. Dickson of the Inland Steel Co., Indiana Harbor, Ind., to whom I extend thanks for investigating this volumetric method.

	Gravimetric method by KOH.	Volumetric.
Steel	0.463	0.460
"	0.890	0.896
"	0.934	0.929
"	1.097	1.101

To show that practically no barium carbonate dissolves during titration, several samples, after being titrated, were filtered and the barium carbonate weighed with the following results:—

Carbon.

Volumetric method.	Gravimetric after titration.
0.89	0.88
0.97	0.97
2.73	2.75
2.75	2.80
3.17	3.20
3.58	3.59
3.84	3.83

Many chemists prefer burning the carbonaceous residue, and I have found that graphite is rapidly oxidised if filtered on a small Gooch crucible, and then without drying or removing the asbestos, the Gooch is immediately placed bottom up in the combustion crucible. Fifteen minutes burning will be ample time, using about 60 c.c. oxygen gas per minute.

I wish to avail myself of this opportunity to thank Mr. H. A. Schwartz, the Secretary of the Indiana Section of the American Chemical Society, for investigating synthetic mixtures of various amounts of dried and also freshly precipitated barium carbonate, when mixed with various amounts of standard barium hydroxide and titrated with acid.

The Aupperle crucible is described in *Iron Age* of October 6, 1904; abstracted in *Iron and Steel Magazine*, December, 1904.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 6th, 1906.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

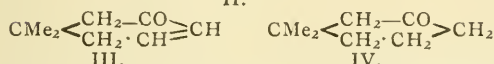
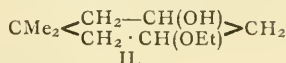
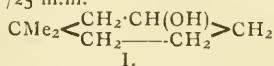
CERTIFICATES were read for the first time in favour of Messrs. George Bagley, Wellington, New Zealand; Frank Baker, B.Sc., St. John's School, Eton; Taylor Cook, B.Sc., 20, Sheddridge Street, Parson's Green, S.W.; Colin Ernest Dall, B.Sc., Maisonette, Maybury Road, Woking; Frederick Alldiss Eastaugh, Forty Hill, Enfield; Edward William Lanchester Foxell, B.Sc., 22, Grand Avenue, Muswell Hill, N.; William Howieson Gibson, B.Sc., 109, Brecknock Road, Holloway, N.; Christopher Maurice Walter Grieb, B.Sc., 33, Torrington Park, Finchley, N.; William Marrs Hooton, M.A., M.Sc., Repton, Burton-on-Trent; Arthur Vivian Hussey, Banthwaite, Belmont, Sutton, Surrey; Ernest Wilfrid Jackson, 65, Douglas Terrace, Middlesbrough; Albert Theodore King, B.Sc., Church Hill, Horsell, Woking; Joseph Martin, B.Sc., Coopers' Company's School, Bow, E.; Otto Oberländer, Ph.D., Chamber of Commerce Buildings, Oxford Court, E.C.; Frederic George Percy Remfry, B.A., D.Sc., Sunnymead, Tenby; Richard Noel Garrod Thomas, B.A., Balliol College, Oxford; Robert Burt Wight, M.A., 3, Clarendon Terrace, Linthorpe Road, Middlesbrough; Mark Arthur Wolff, 6, Hanover Terrace, Holland Park, W.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Richard Abegg, Ph.D.; Paul Seidelin Arup, M.A.; William Heath Bayliss; Oscar Walter Bethea; James Spears Broome, B.Sc.; Thomas Henry Byrom; John Carmichael; Percy Henry Carpenter; Charles Taylor Cockburn; Reginald de Vere Cornwall; Hubert Frank Coward, M.Sc.; Henry Ernest Crocker; Archibald Prideaux Davson; James Herbert Dinwoodie; Charles George Edgar Farmer; Samuel Field; Anthony Nisbet Fitzgerald, B.A., B.Sc.; David Paton Grubb, B.Sc.; Octavius Hall, L.R.C.P., L.R.C.S.; John Hamer; H. Norman Hanson; Frederick James Harris; Charles Percy Hines, B.Sc.; Archibald McArthur Johnston; Edward Rees Jones; William Richard Simpson Ladell; David McIntosh, B.Sc.; Tarak Nath Majumdar; John Mastin; Alexander Edmund Middleton; Arthur Higgs Morris; George Naylor; Arthur Percival Newton, B.Sc.; Charles Harold Oxland, B.Sc.; Benjamin Dawson Porritt; Herbert Stanley Redgrove; Frederic Ion Richardson, B.A.; Reginald Ernest Robinson, B.A.; Gopal Chandra Sen, M.A.; John Lionel Simonsen, M.Sc.; Charles Smith; William R. R. Starling; Harry George Telling; Emmanuel Isaac Thorne; George Gordon Watt; Frederick William Watson, B.Sc.; Chr. Winther, Mag. Scient.

Of the following papers, those marked * were read:—

*212. "Action of Reducing Agents on 5-Chloro-3-keto-1:1-dimethyl-Δ⁴-tetrahydrobenzene." By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

Experiments have proved that chloroketodimethyltetrahydrobenzene behaves in a varied manner towards reducing agents. Thus, sodium in moist ethereal solution (*Trans.*, 1905, lxxviii., 1494) gives, as main product, 3-hydroxy-1:1-dimethylhexahydrobenzene (I.), whereas sodium in absolute alcoholic solution yields a small amount of this alcohol, and to a much larger extent 3-hydroxy-5-ethoxy-1:1-dimethylhexahydrobenzene (II.), as a colourless liquid boiling at 135°/25 m.m.



When the chloroketone is treated with zinc filings in aqueous alcoholic solution, either in the cold or on heating, 3-keto-1:1-dimethyl-Δ⁴-tetrahydrobenzene (III.) is formed as a colourless liquid boiling at 88°/32 m.m., and possessing an odour of almonds and camphor. On the other hand, zinc dust in either glacial or dilute acetic acid gives rise to 3-keto-1:1-dimethylhexahydrobenzene (IV.), boiling at 77°/5°/27 m.m., and having a pungent camphoraceous odour.

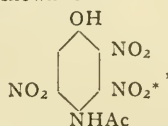
Characteristic derivatives of these various substances have been prepared, and in all cases their constitution has been conclusively proved by the oxidation products obtained from them.

In every reduction, dicyclic compounds are formed in addition to the simple ring compounds, and the following have been isolated, and were described together with some of their derivatives:—

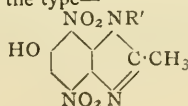
3:3'-Diketo-5:5':5':5'-tetramethyl-Δ¹:1'-dicyclohexene (m. p. 178°); 1:1'-dihydroxy-5:5':5':5'-tetramethyl-Δ²:2'-dicyclohexene (m. p. 148°); 1:1'-dihydroxy-5:5':5':5'-tetramethyldicyclohexane (m. p. 212°); 3:3'-dihydroxy-5:5':5':5'-tetramethyldicyclohexane (m. p. 183°).

*213. "A New Trinitroacetaminophenol and its Use as a Synthetical Agent." By RAPHAEL MELDOLA.

When diacetyl-*p*-aminophenol is nitrated by dissolving it in cold fuming nitric acid the first product is the mono-nitro-derivative, C₆H₃(OAc)(NO₂)·NHAc=1:3:4, corresponding to the *m*-nitro-*p*-aminophenol of Hähle (*Four. Prakt. Chem.*, 1891, [ii.], xliii., 63; Reverdin and Bucky, (*Ber.*, 1906, xxxix., 2687). This mononitrodiacetyl compound can be further nitrated by dissolving it in a mixture of fuming nitric and strong sulphuric acids, when a trinitroacetaminophenol is produced which forms the subject of the paper communicated by the author. This trinitro-derivative, which has not hitherto been described, is remarkably active as a synthetical agent owing to the extreme mobility of one of the nitro-groups. It crystallises in yellow needles melting with decomposition at 178—179°. The constitution is shown to be—



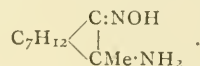
the nitro-group marked * being the mobile group. The action of various amines on the trinitro-compound has been studied, and the final products shown to be substituted benzimidazoles of the type—



where R' is the radicle present in the amine used. In some cases substituted diaryl- or alkylaryl-amines are formed as intermediate products, and these undergo "anhydridisation" on heating or on treatment with dehydrating agents. The trinitro-compound reacts also with hydrazines and with certain phenolic substances, the investigation of the products being still in hand.

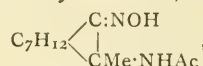
*214. "Pinene Nitrolamine." By FREDERICK PEACOCK LEACH.

Pinene nitrosochloride, when allowed to remain at 45—50° with ammonia and alcohol, gives a well crystallised nitrolamine,—



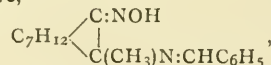
This compound melts somewhat indefinitely at 123—125°, contains approximately 3H₂O, and crystallises from alcohol in long silky needles.

The hydrochloride, oxalate, and platinichlorides have been prepared; the acetyl derivative,—



crystallises in hexagonal prisms melting at 224°; the dibenzoyl derivative melts at 167°, and the diphenyl-carbamide at 133°.

Pinene nitrolamine reacts very readily with aldehydes, giving well crystallised condensation products; the benzylidene derivative,—

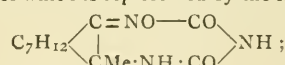


melts at 162°; the salicylidene derivative at 128°, and the furfurylidene derivative at 164°.

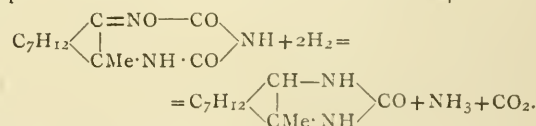
With reducing agents either no action takes place or the amino-group is eliminated, giving rise to the ketone (Wallach's pinocamphone), which has been identified by means of its oxime melting at 86°.

*215. "A Pseudo-semicarbazide from Pinene." By FREDERICK PEACOCK LEACH.

Potassium cyanate and pinene nitrosochloride interact in alcoholic solution, giving a compound, C₁₂H₁₇O₂N₃, the constitution of which is represented by the formula,—



it crystallises from alcohol in rosettes of prisms melting at 238—240°, dissolves in dilute alkalis, and gives alkali salts. When reduced with zinc dust and dilute acetic acid, a pseudo-carbamide is obtained which melts at 224°:—



Concentrated sulphuric acid gives pinene nitrolamine, carbon dioxide, and ammonia. The action of nitrous acid converts the pseudo-carbamide into a nitroso-compound, which crystallises from alcohol in yellow plates with a pink lustre and melting at 161°; this on reduction gives a pseudo-semicarbazide melting at 209°, from which by the action of aldehyde and ketones several of the ψ -semicarbazones have been prepared and analysed.

216. "Some Derivatives of Benzophenone. Synthesis of Substances occurring in Coto-bark." (Preliminary Notice). By WILLIAM HENRY PERKIN, Jun., and ROBERT ROBINSON.

A mixture of veratryl chloride and pyrogallol trimethyl ether suspended in carbon disulphide reacts readily with aluminium chloride with the formation of 1:2:3:3':4'-pentamethoxybenzophenone, (MeO)₂C₆H₃·CO·C₆H₂(OMe)₃, which crystallises from alcohol in prisms and melts at 125°. If, however, the reaction is prolonged, the product contains

hydroxytetramethoxybenzophenone, which crystallises in needles, melts at 115° , and is readily separated from the pentamethoxy-derivative on account of its solubility in alkalis.

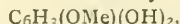
When hydroxytetramethoxybenzophenone is treated with benzoyl chloride and caustic potash it yields a benzoyl derivative which crystallises from alcohol in stout, colourless prisms, melts at 149° , and is converted into pentamethoxybenzophenone when it is treated with methyl sulphate and caustic potash.

2 : 4 : 6 : 3' : 4'-Pentamethoxybenzophenone (pentamethylmaclurin), $(\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OMe})_3$, is obtained when aluminium chloride reacts with a mixture of veratryl chloride and phloroglucinol trimethyl ether in the presence of carbon disulphide. It melts at 156 —to 157° and yields a monobromo-derivative (m. p. 144°) when its solution in chloroform is treated with bromine, and there can be no doubt that it is identical with the substance which Ciamician and Silber (*Ber.*, 1892, xxv., 1132) obtained from protocotin, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OMe})_3$, by substituting two methyl groups for the methylene group.

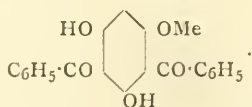
Since 2 : 4 : 6 : 3' : 4'-pentamethoxybenzophenone is pentamethylmaclurin, many attempts were made with the object of converting it into maclurin itself, but so far without success.

3' : 4'-Methylenedioxy-2 : 4 : 6-trimethoxybenzophenone, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OMe})_3$, was next synthesised by treating a mixture of piperonyl chloride and phloroglucinol trimethyl ether in carbon disulphide solution with aluminium chloride. The substance so obtained melted at 133° and was identical with the oxyleucotin of coto-bark, as was shown by a careful comparison of the two preparations and by the fact that when they were mixed in equal quantities the melting point was the same as that of the constituents.

When phloroglucinol monomethyl ether, —



is treated with benzoyl chloride in the presence of zinc chloride, 2 : 4-dibenzoxy-6-methoxy-m-phthalophenone, $(\text{C}_6\text{H}_5\cdot\text{CO})_2\text{C}_6\text{H}_3(\text{OMe})(\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_5)_2$, (m. p. 130 — 135°) is produced. This substance is readily hydrolysed by alcoholic potash with the formation of 2 : 4-dihydroxy-6-methoxy-m-phthalophenone, $(\text{C}_6\text{H}_5\cdot\text{CO})_2\text{C}_6\text{H}_3(\text{OMe})(\text{OH})_2$, which melts at 187° , and is also produced when cotoin dibenzoate is treated with benzoyl chloride and zinc chloride. Its constitution must therefore be represented by the formula—



217. "The Liquid Volume of a Dissolved Substance." By JOHN SCOTT LUMSDEN.

The values deduced for atomic volumes and atomic refractions from experiments made on pure liquids, hold with fair accuracy when applied to solids and liquids in solution; and the inference is that a liquid retains its own volume when dissolved, and that a solid assumes in solution the volume which the same weight of it would have if it existed as a liquid at the same temperature. If this inference is correct, a law of the "liquid volume" of a dissolved substance is made evident, and experimental results are recorded which prove that there is such a law which holds, not only for the volume assumed by a solid and liquid, but also for the volume occupied by a dissolved gas.

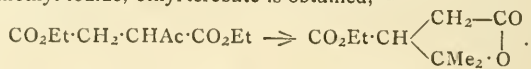
The law is expressed as follows:—When a substance in the liquid state dissolves without change of volume, the same substance when in the state of solid or gas will, when dissolved in the same solvent, change to the volume which the same weight of it would have if it were a pure liquid at the temperature of solution.

Irregularities are proved to be due to the experimentally ascertained facts that the volume in solution varies slightly with the solvent and with the degree of concentration of

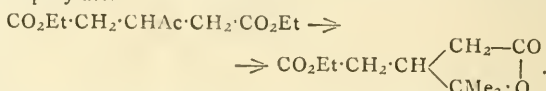
the solution, and also from the circumstance that when a liquid is dissolved there is often a slight alteration in volume, but the deviation from accuracy from these causes is so small that the law deserves recognition as a guide when problems relating to solution in non-dissociating solvents are being dealt with.

218. "A Synthesis of Terebic, Terpenylic, and Homoterpenylic Acids." By JOHN LIONEL SIMONSEN.

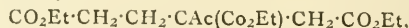
When ethyl acetylsuccinate is treated with magnesium methyl iodide, ethyl terebate is obtained,—



In a similar manner by the action of magnesium methyl iodide, ethyl β -acetylglutarate is converted into ethyl terpenylate.

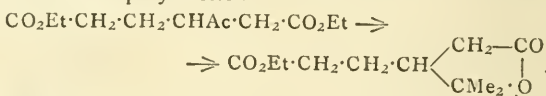


When the sodium derivative of ethyl acetylsuccinate is treated with ethyl β -iodopropionate, ethyl β -acetylbutane- $\alpha\beta\delta$ -tricarboxylate,—



boiling at 200 — $201^{\circ}/14$ m.m. is obtained.

This ester, when hydrolysed with concentrated hydrochloric acid, gives β -acetylglutaric acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHAc}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which melts at 102° and yields an ethyl ester boiling at $179^{\circ}/18$ m.m. which, when treated with magnesium methyl iodide, is converted into homoterpenylic ester.



This, on hydrolysis, yields homoterpenylic acid (m. p. 100 — 101°), which is identical with the homoterpenylic acid obtained by Baeyer (*Ber.*, 1896, xxix., 1919) by the oxidation of pinene.

219. "Influence of Light on Diazo-reactions." Part I. By KENNEDY JOSEPH PREVITÉ ORTON, JOSEPH EDWARD COATES (and, in part, FRANCES BURDETT).

Solutions of diazonium salts in water, methyl or ethyl alcohol, acetic or formic acid, decompose rapidly on exposure to light, although in many cases they may be preserved for long periods if kept in the dark (compare *Proc.*, 1905, xxi., 168).

The product of the reaction depends on the solvent; in aqueous solution a phenol is formed; in methyl or ethyl alcohols, the corresponding phenyl, methyl, or ethyl ether is mainly produced, in some cases a certain amount of the diazonium salt being at the same time converted into hydrocarbon (replacement of the diazo-group by hydrogen); in acetic acid solution, a phenyl acetate is the sole product, but in formic acid, the change follows the equation: $\text{Ar}\cdot\text{N}(\text{X})\text{:N} + \text{H}\cdot\text{CO}_2\text{H} = \text{ArH} + \text{N}_2 + \text{CO}_2 + \text{HX}$.

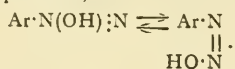
In most cases these reactions are quantitative; further, many diazo-compounds, which do not yield phenols, ethers, or phenyl acetates (for example, *s*-tribromodiazobenzene), when solutions in the appropriate solvents are heated, can be readily induced by light to undergo these changes.

Solutions of diazotates (*isodiazotates*) are not affected by light.

High concentrations of acid (for example 25 per cent sulphuric acid) do not appreciably affect the rate of decomposition of the diazonium salts. Exposure to light of solutions of diazonium sulphates in 95 per cent sulphuric acid brings about a conversion into the corresponding phenol.

These facts would appear to render untenable the view (Hantzsch) that phenols are formed from *syn*-diazo hydroxides, since it is difficult to see how in such strongly

acid solutions there can be any hydrolysis of the diazonium salt and consequent formation of the diazonium hydroxide to allow of their presence, thus :—



220. "*The Viscosity of Liquid Mixtures.*" By ALBERT ERNEST DUNSTAN and ROBERT WILLIAM WILSON.

In continuation of previous work on this subject the authors have investigated the viscosity concentration curve of mixtures of water and sulphuric acid.

They find a well-defined maximum point corresponding with $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$, and a minimum corresponding with $3\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$.

The general behaviour of solutions from the point of view of viscosity was discussed, and it was shown how, from a knowledge of the viscosity and the chemical series to which it belongs, it is possible to determine the molecular weight of a liquid.

NOTICES OF BOOKS.

Numerical Tables and Constants in Elementary Science. By SYDNEY LUPTON, M.A., F.C.S. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1906.

THIS collection of tables of scientific data is probably too well known to require recommendation, for it has been widely used now for more than twenty years. In conciseness and completeness it is unique, and as it has recently been thoroughly revised it must be regarded as an indispensable part of the equipment of scientific libraries. The tables and miscellaneous data are classified according to the sciences with which they are connected, and as a good index is provided the book is very convenient for reference. The results of some of the most recent determinations of various constants are now included in an appendix, and many corrections and alterations have been made, while the full notes and references to standard works will give great assistance to those who wish to look up further information.

A Method of Teaching Chemistry in Schools. By A. M. HUGHES, B.Sc. (Lond.), and R. STERN, B.Sc. (Lond.). Cambridge: The University Press. 1906.

THERE is a great deal of good material in this book, and a teacher will get many hints from it, but at the same time the general plan advocated by the authors hardly seems satisfactory. For one thing, too many substances are introduced, and the arrangement is somewhat disjointed, while no single phenomenon is studied with anything resembling thoroughness. It is generally recognised that the aim of scientific teaching is the inculcation of a habit of thought, and this experience shows can only be effected by setting a high ideal of patience and accuracy before the learner. With a good teacher a detailed study of combustion, for instance, can provide material for weeks of work, with the short time usually allotted to science, and at the end of that period the child should have gained some idea what research means, though it must be allowed that he would have very little acquaintance with most of the compounds with which he would meet according to this scheme. The arguing from known to unknown is of course a good feature of the book, but the earlier parts want much enlarging; for instance, no corrections for temperature and pressure in measuring gases are explained. Nevertheless, some of the experimental directions will suggest useful ideas for the arrangement of apparatus, and the introduction is worth the careful attention of teachers.

Über Kathodenstrahlen. ("On the Cathode Rays"). By P. LENARD. Leipzig: Johann Ambrosius Barth. 1906.

THIS pamphlet contains the text of the Nobel Lecture delivered at Stockholm before the Royal Swedish Academy of Sciences in May, 1906, and gives an interesting historical review of the cathode rays. Those who wish to learn something of modern theories of the constitution of matter, radio-activity and the nature of the electrons, without going very deeply into the subject, will find this short lecture gives them exactly what they want—a clear and readable account of the development of our present ideas, in which the reader is supposed to possess the minimum of previous knowledge of physics and mathematics. The author has taken special care to refer to all publications which treat of recent advances, and expressly states that he has given special prominence to his own work and theoretical views, believing that he is thus considering the wishes of his audience; at the same time, he scrupulously ascribes the honour of discoveries to those whose right it is to receive it. Altogether it would be difficult to find a more interesting and lucid discussion of the subject.

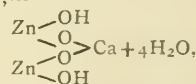
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 23, December 3, 1906.

The Reduction of the Oxide of Chromium by Boron.—Binet de Jassonneix.—Former experiments have shown that when chromium is heated with boron in the electric furnace in a charcoal crucible, a fused body results, containing the definite boride CrB ; and according to all of these, the compound exhibited great resistance to chemical reagents. The author obtained very different results by reducing the oxide of chromium with boron in the electric furnace, in crucibles of magnesium. The process gives fused products of variable composition, containing the definite boride CrB , which represents the limit of saturation of chromium by boron. All the products are attacked by hydrofluoric, hydrochloric and sulphuric acids, with formation of boric acid; nitric acid and solutions of the alkalis produce no effect. They can be oxidised at a high temperature by the fused alkalis or alkaline carbonates. Analysis shows that the content of CrB in the products obtained varies from 5 per cent to 17 per cent, and there is also boron in the state of the carbide.

A very Sensitive Method of Precipitating Zinc.—Gabriel Bertrand and Maurice Javillier.—The method originated in an observation, which led one of these authors, in 1892, to prepare crystalline compounds of zinc oxide with the metals of the alkaline earths. A crystalline deposit was obtained by distilling the commercial liquid ammonia with soapmakers' alkali, which proved to be zincate of calcium,—

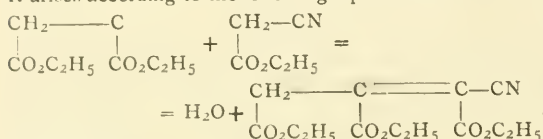


the probability being that the zinc arose from the soda-lye. This production of zincate of calcium seemed to afford a very sensitive means of detecting zinc; zincate of calcium was prepared by adding excess of ammonia to a solution containing zinc and calcium, boiling, and allowing to stand till the crystals were deposited; these are so little soluble in the presence of lime, that even traces of zinc contained in a large quantity of liquid can be extracted; the calcium was precipitated as oxalate, and the zinc remaining in solution was converted into sulphate and weighed. The results obtained showed that the zinc recovered at the end of the experiment was from 88 to 97 per cent of the amounts

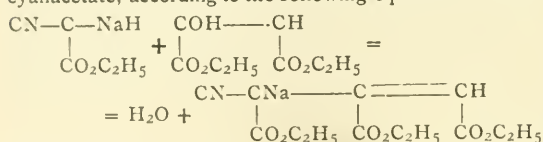
originally introduced. The new method therefore yields zinc almost quantitatively from very dilute solutions.

The Etherification of Arsenious Anhydride by the Alcohols and Phenol.—V. Auger.—This research followed upon the observation that arsenious anhydride is not volatile with water vapour, whilst it passes over in considerable quantity with the vapour of methyl alcohol, the explanation of which phenomenon seemed to point to the formation of a methyl-arsenious ether. The author has already demonstrated that arsenic acid heated with glycerine readily furnishes an arseniate, very unstable in the presence of water; and it seemed probable that the simple alcohols would act similarly with arsenious anhydride, but furnishing very little of the ether, in consequence of the hydrolysing action of the water formed during the process. The alcohol was heated with excess of crystallised arsenious anhydride, and the arsenic remaining in the liquid unchanged estimated with iodine. In this way were obtained the arsenites of the following alcohols: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and isoamyl.

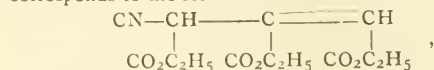
Condensation of Oxalacetic Ether with Cyanacetic in presence of Piperidine.—Ch. Schmitt.—The author has previously described the conditions of studying the condensing action of the amines upon the cyanacetic ethers in presence of the ketone ethers (*Comptes Rendus*, cxl., p. 1400, May 22, 1905). Continuing the investigation, he has produced the crystalline body $C_{13}H_{17}O_6N$. It arises according to the following equation:—



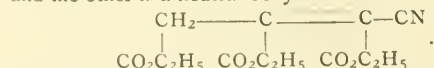
which is ethyl cyanopropenetricarboxylate. It is a neutral body, losing CO_2 under the action of acids and alkalis, but forming no definite product. This differs from a body of the same empirical formula, described by J. Errera and E. Perciabosco as a heavy yellow oil with an acid reaction. A new synthesis of the latter has thrown light upon its constitution. Ethyl oxalacetate reacts upon ethyl sodium cyanacetate, according to the following equation:—



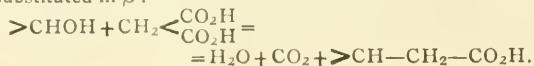
and the latter body loses its nitrite group, when treated with hydrochloric acid, giving rise to aconitic acid. To sum up; two distinct derivatives of cyanacetic ether exist, of formula $C_3H_7O_6N$; the one has an acid reaction, and corresponds to the formula—



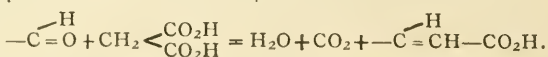
and the other is a neutral body of the formula—



Replacement of the Hydroxyl of certain Carbinols by the Radical $-\text{CH}_2\text{CO}_2\text{H}$.—R. Fosse.—The hydroxyl of the secondary aromatic carbinols, substituted by the residues CH_3-O , CH_2-O , CH_3-O , CH_3-O , is readily replaceable by the ethyl radical, $-\text{CH}_2-\text{CO}_2\text{H}$. These hydroxyl compounds and malonic acid give up 1 molecule of water and of CO_2 , producing a new series of propionic acids, substituted in β :—



This is a new reaction, resembling the well-known one of the aldehydes and malonic acid, which leads to the propionic acids substituted in β :—



The author then gives an account of several $\beta\beta$ -propionic acids prepared by him according to this method.

MISCELLANEOUS.

Institute of Chemistry.—Examination in Biological Chemistry, October 23rd to 26th, 1906.—Two Associates examined for the Certificate passed—Robert William Clarke, A.I.C.; Reginald Mead Filmer, B.Sc. (Lond.), A.I.C. Two Candidates examined for the Associateship passed—Conrad Theodore Gimmingham, University College, London; Wilfred Ambrose Whatmough, King's College, London, and under A. H. M. Muter, F.I.C.

Carbohydrates of Tea.—A. D. Maunbrecher and B. Tollens.—The dried substance contains an average of 5.60 per cent of pentosan.—When the caffeine is removed by extraction with water, traces of fructose are found in the syrup thus obtained, and also glucose. Hydrolysis of the residue from the extraction with water revealed the presence of arabinose and galactose.—*Berichte*, xxxix., No. 14.

MEETINGS FOR THE WEEK.

THURSDAY, 27th.
SATURDAY 29th

Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Signalling to a Distance, from Primitive Man to Radiotelegraphy" (Experimentally Illustrated), by W. Duddell, M.Inst. E.E.

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THE CHEMICAL NEWS.

Vol. XCIV., No. 2457.

CALCIUM AS AN ABSORBENT OF GASES, AND ITS APPLICATIONS IN THE PRODUCTION OF HIGH VACUA AND FOR SPECTROSCOPIC RESEARCH.*

By FREDERICK SODDY, M.A.

By means of a special electric furnace, surrounded by a porcelain tube and enclosed within a glass tube, it has been found possible to heat reagents *in vacuo*, in sealed soft glass apparatus, to a far higher temperature than the softening point of glass. Calcium, heated in this manner, is, under suitable conditions, an absorbent of all the known gases, with the exception of those of the argon group. Provided the initial gas-pressure does not exceed a few millimetres of mercury, all the common gases are rapidly and completely absorbed by calcium between 700° and 800° C., and a vacuum attained through which the electric discharge cannot be forced. Arndt (*Ber.*, 1904, xxxvii., 4733), in an investigation of the melting-point of calcium, noticed that the calcium volatilised freely below its melting-point when heated in a vacuum, and the vapour reacted energetically with the oxygen and nitrogen of the residual air. He did not investigate the behaviour of other gases.

Barium and strontium behave in a manner very similar to calcium.

The high vacua readily produced by the absorption of residual gases by calcium are at least equal to the highest attained by any other process. By filling the apparatus with mercury after the action of the calcium, and compressing any residual gas several hundred times into a tiny spectrum tube, it was found that the vacuum was still so high that the spectrum tube was of high resistance and fluoresced brightly under the discharge. Since argon is not absorbed, the air must be first removed from the apparatus by means of a Fleuss pump, and by replacement of the last traces with some argon-free gas, before the calcium is brought into action. The condensed gases evolved from the apparatus on heating usually suffice to replace the last of the air during the mechanical exhaustion. The calcium, being a good conductor of electricity, may be readily heated to the required temperature within the sealed glass vessel by induction through the walls from an alternating circuit outside the vessel.

By admitting known volumes of air, and absorbing all but the argon, it was found that it was not possible to force a discharge through argon at a pressure less than 1/50 m.m. of mercury. At this pressure the orange and green lines of the spectrum became faintly visible, and at 1/25 m.m. the reds appeared. At 1/3 m.m. the spectrum tube had a resistance equivalent to 5 m.m. alternative spark-gap in air, and at 1 m.m. the tube was still brilliantly fluorescent. The other inert gases behave similarly. Helium is non-conducting below a pressure of 1/20 m.m. when pure, but in the presence of any common gas, as hydrogen or oxygen, one-hundredth of this amount serves to reveal the D₃ line. This behaviour of the inert gases explains why they appear to "run out" in spectrum tubes so quickly, for when the traces of common gases always present are absorbed by the electrodes, the inert gases are left in the pure and non-conducting state. The apparent ease with which high vacua are obtained by the use of cooled charcoal is misleading, for the atmospheric helium and neon,

although not conducting the discharge, remain unabsorbed. To any but an electrical test "charcoal vacua," like "calcium vacua," are poor, unless precautions are taken to remove air before the absorption.

ADDENDUM.—A Method of Gauging by Evaporation the Degree of High Vacua.

By ARTHUR JOHN BERRY.

The attempt was made to use the rate of evaporation of liquid air in a Dewar bulb as an indication of the degree of vacuum therein. The same bulb was exhausted by three methods: (1) by the mercury pump; (2) by cooled charcoal from atmospheric pressure, using two successive quantities of charcoal; (3) by cooled charcoal after the air had been first removed by a pump. It was found that whereas the vacuum in (2) was inferior to that in (1), that in (3) was very much the best of the three.

THE ESTIMATION OF CADMIUM AS THE OXIDE.

By CHARLES P. FLORA.

CADMIUM may be simply and accurately estimated by converting the carbonate to the oxide by ignition. The oxide of cadmium may be subjected to very intense heat without loss from volatilisation; but in the presence of any carbonaceous matter it is very easily reduced to the metal, which is quite volatile at high temperatures. Consequently, this method has always been subject to more or less change of error where paper-filters have been used. The usual course has been to wash thoroughly and then dry the precipitated carbonate, which is then removed as completely as possible from the filter; the latter then being burned separately. Even here there has always been a very appreciable loss, to avoid which various more or less complicated modes of treatment have been offered. As a type of these, we may take that of Max Muspratt (*Journ. Soc. Chem. Ind.*, 1894, xiii., 211), who, after noting that high results were given by the ignition of the nitrate formed by dissolving the precipitated carbonate in nitric acid on account of included sulphate, proceeded as follows:—The precipitated carbonate was washed and dried, and as completely as possible scraped free from the filter-paper, and then converted to the oxide by gentle ignition. This carbonate was entirely free from sulphate. The filter-paper was treated with nitric acid, and the resulting solution and rinsings brought into a large porcelain crucible and evaporated to dryness. The dry nitrate was gently heated, and the weight of the oxide obtained added to that of the mass of the precipitate. Even after this tedious procedure, Muspratt is obliged to suggest that the results would be more satisfactory if the oxide obtained by the ignition of the paper and the residues upon it be calculated as Cd₂O rather than CdO. Evidently the method would give satisfactory results if this reducing action of the filter could be avoided, and in former papers from the Kent Chemical Laboratory of Yale University, it has been shown that this may be accomplished by the use of asbestos filters in a Gooch crucible (see Browning, *Am. Journ. Sci.*, 1893, [3], xlvii., 280; Browning and Jones, *Ibid.*, 1896, [4], ii., 269). There is then no danger of loss from reduction, and the carbonate method is simplified and placed among the good analytical methods. Recently, however, Miller and Page (*CHEMICAL NEWS*, 1901, lxxxiv., 312) have found that "the carbonate method is the most troublesome and the least satisfactory"; but these investigators did not use the asbestos filter.

The work of the writer upon the carbonate method fully substantiates the previous work from this laboratory. For the determinations given, a solution of cadmium sulphate was used, whose standard was accurately given by the

* Abstract of a Paper read before the Royal Society, November 15, 1906.

average of a large number of closely agreeing electrolytic determinations. Portions of this solution were accurately measured from a burette and diluted to 300 c.c. with hot water. A 10 per cent solution of potassium carbonate was then added, drop by drop, with constant stirring until no further precipitation took place. The whole was then boiled for about fifteen minutes, when the precipitate became granular and quickly settled. It was then filtered upon an asbestos mat in a Gooch crucible, which had previously been ignited and weighed, and was then carefully washed with hot water. In several cases, washing by decantation was used. The precipitate was then dried and ignited over a Bunsen burner, first gently, then at full red heat until a constant weight was obtained, care being taken to avoid the reducing action of any unburned gas from the burner. The following results were obtained:—

No.	CdO taken.	CdO found.	Error.
	Grm.	Grm.	Grm.
1.	0.1277	0.1275	-0.0002
2.	0.1277	0.1280	+0.0003
3.	0.1277	0.1272	-0.0005
4.	0.1399	0.1391	-0.0008
5.	0.1399	0.1399	0.0000
6.	0.1703	0.1700	-0.0003
7.	0.1703	0.1700	-0.0003
8.	0.2129	0.2128	-0.0001
9.	0.2129	0.2128	-0.0001
10.	0.2554	0.2554	0.0000

The method is simple in execution, and the above results prove its accuracy.

Some of the older manuals also give as a method for the estimation of cadmium that of igniting to the oxide the precipitated hydroxide obtained by adding a solution of sodium or potassium hydroxide to the solution containing the salt of cadmium. Follenius (*Zeit. Anal. Chem.*, 1874, xiii., 284) has published some results obtained with the use of an asbestos filter, and it was decided to try this method in comparison with the carbonate method. As in the experiments with the carbonate, portions of the solution of cadmium sulphate were carefully measured off from a burette, diluted to about 300 c.c., and heated to boiling. A 10 per cent solution of potassium hydroxide was then added drop by drop and the whole boiled for about fifteen minutes. Upon cooling, the precipitation quickly settled in a semi-granular state, and was best filtered and washed by decantation. The results were lower than when the cadmium was precipitated as the carbonate, as is shown by the following table:—

No.	CdO taken.	CdO found.	Error.
	Grm.	Grm.	Grm.
1.	0.1277	0.1277	0.0000
2.	0.1277	0.1270	-0.0007
3.	0.1277	0.1260	-0.0017
4.	0.1277	0.1286	+0.0009
5.	0.1362	0.1350	-0.0012
6.	0.1399	0.1389	-0.0010
7.	0.1703	0.1697	-0.0006
8.	0.1403	0.1693	-0.0010
9.	0.1703	0.1699	-0.0004
10.	0.1788	0.1802	+0.0014
11.	0.2129	0.2139	+0.0010
12.	0.2129	0.2128	-0.0001

While the figures show that fair results may be obtained by the hydroxide method, it can be compared with the carbonate method neither for accuracy nor convenience; the precipitate does not attain the same granular form as that of the carbonate; it is hard to filter, difficult to wash, and can be removed completely from the beaker in which precipitation takes place only with the utmost difficulty.—*American Journal of Science*, xx., p. 456.

REACTION OF SALTS OF COBALT OF SERVICE IN ANALYTICAL CHEMISTRY.*

By Prof. E. PINERUA ALVAREZ.

In studying the salts of cobalt, I have succeeded in verifying, without noticing the observations or experiments of Reichel, Winkler, and Donath (1901), that with the hydrates of sodium and potassium in great excess, they give a liquid of a very intense blue colour, especially when heated.

The study of this blue liquid proved to be an alkaline solution of cobaltous anhydroxide of a blue colour (CoO).

By the action of soda in concentrated solution, the pink cobaltous hydrate loses its water, turns blue, and on dissolving it in excess of soda the solution acquires the same blue colour.

The dehydration of the cobaltous hydrate $\text{CoO} \cdot \text{H}_2\text{O} = \text{CoO}_2\text{H}_2$ is produced not only by soda, but also by caustic baryta, anhydrous calcium chloride, and other substances with an affinity for water, changing it always from pink to blue.

This solution, of beautiful blue colour, is decolorised by the action of water, by hydrolysis of the alkaline cobaltous compound or cobaltite which is formed, CoO_2K_2 , giving back the original hydrate, $\text{Co}(\text{OH})_2$, or other polymeric hydrates with variable formulae, and colours which oscillate between intense pink and whitish pink, according to the concentration of the alkaline solution and the temperature.

The reaction is so sensitive that it may be used in analysis.

It is enough to add a drop of a solution diluted to 1 per cent of cobaltous chloride or sulphate to a great excess of the boiling saturated solution of potash or soda, in order to obtain the said blue liquid.

In the presence of a large quantity of nickel salts the precipitate obtained acquires a bluish tint as perceptible as for the small quantity of cobalt.

This blue coloration should not be confounded with that of the compound precipitated by adding in the cold soda or potash to solutions of cobaltous salts. This precipitate, which turns pink on heating, gives the blue liquid if a fragment of sodium or potassium hydrate is added, heating afresh until the alkaline solution is sufficiently concentrated.

THE NITROMETER.

By J. NEWFIELD and J. S. MARX.

HAVING occasion to use the nitrometer extensively in our work we have made a study of some of the factors which affect the results obtained by means of this instrument, especially with reference to its use in the analysis of nitrocellulose and other explosives. We have used the form known as Lunge's improved nitrometer or gas volumeter.

A description of this apparatus is very well given in Sutton's "Volumetric Analysis," eighth edition, pages 616 to 618. It consists in brief of a decomposing bulb connected by a heavy rubber tube to an overflow. By means of a small piece of rubber tubing this bulb can be connected to a long measuring tube graduated to tenths of cubic centimetres. Temperature and barometric corrections are dispensed with by having a closed tube inserted between the measuring tube and its overflow, all three being joined together by means of a rubber tube. In this sealed tube are 100 c.c. of air over mercury at 760 m.m. pressure and 0° C. temperature. Thus when the volume of air in the tube is 100 c.c. and the mercury column levelled with that in the measuring tube, its gas is also under the same conditions of temperature and pressure,

* Note presented at the Sixth International Congress of Applied Chemistry, held at Rome, 1906.

However, it would be difficult and also unnecessary to obtain just 100 c.c. of air in the sealed tube under standard conditions, so a factor is obtained in the following way:—Approximately 100 c.c. of air are introduced into the sealed tube, then a weighed portion of perfectly pure, dry potassium nitrate is run through the apparatus. From its composition 1 gm. of the nitrate gives 221 c.c. of nitric oxide gas, under normal conditions. The difference between 221 c.c. and what is actually obtained by experiment "fixes" the factor which is used in all subsequent determinations. About 40 to 50 c.c. of sulphuric acid are used in making a determination.

Effect of Sulphuric Acid of different Concentrations.

Strength of acid (per cent).	Cubic centimetres of NO per gm. KNO ₃ .
97.18	221.11
96.59	221.08
94.81	221.09
94.05	221.10
93.02	221.60
90.96	223.43
85.20	223.61

As the original factor is fixed by the use of potassium nitrate, these results only indicate that changes in the concentration of the acid between 97 and 94 per cent are without effect, but a weaker acid gives too high results, probably because it absorbs less of the nitric oxide. That the stronger acid absorbs nitric oxide was shown by the following experiments:—On agitating 112 c.c. of nitric oxide with 40 c.c. of sulphuric acid of 97 per cent for three minutes, 1 c.c. or 0.89 per cent was absorbed. On shaking 112 c.c. with 40 c.c. of an acid of 85 per cent, 0.5 c.c. or 0.45 per cent was absorbed.

Determinations made with acid from 85 to 50 per cent gave widely varying results, indicating that reliable values can not be obtained with such weak acids.

In the analysis of nitrocellulose and similar explosives the strength of the acid is even more important, as will be seen from the following table:—

Strength of acid (per cent).	Cubic centimetres of nitric oxide per gm. cellulose.
97.18	199.5
96.59	199.5
94.81	199.7
94.05	197.1
93.02	193.1
88.60	147.5

Here it is evident that an acid weaker than 94.8 per cent does not effect a complete decomposition of the nitro-cellulose, probably because the weaker acids do not completely dissolve the guncotton.

Effect of Temperature.—Between 15° and 40° the temperature at which the decomposition is effected is without appreciable effect on the results obtained either with potassium nitrate or with nitro-cellulose. At 40° or above, loss of nitric acid or oxides of nitrogen occurred on the addition of the sulphuric acid, causing low results.

Effect of Time of Agitation.—The following results were obtained with acid of 97 per cent at 15°.

Time of agitation (minutes).	Cubic centimetres of NO per gm. KNO ₃ .	Cubic centimetres of NO per gm. nitro-cellulose.
1	221.07	200.8
2	220.89	—
3	220.98	201.9
5	220.97	201.8
8	220.92	201.8

It seems that a complete decomposition of the potassium nitrate is secured in one minute, while three minutes should be used for nitro-cellulose.

Effect of Pressure.—The following results were obtained with acid of 97 per cent at 15° C., the pressure being

roughly calculated from the difference in heights of the mercury columns in the decomposing and overflow bulbs.

Pressure (pounds per square inch).	Cubic centimetres of NO gas per gm. KNO ₃ .
7	221.73
14 (normal)	221.03
30	219.95

It is seen from the above that the pressure at which the gas exists exerts a marked effect on the results obtained. This is explained by the fact that the higher the pressure exerted on the gas, the more nitric oxide is dissolved in the sulphuric acid. Always keeping the gas at a slightly reduced pressure appears to give very satisfactory and accurate results.

Effect of Standing dissolved in Sulphuric Acid.—Experiments were carried on with the aim in view of determining if there is any marked difference in results to be noted when organic nitrogenous bodies are allowed to remain for some time in sulphuric acid before decomposing in the nitrometer instead of immediately decomposing as is the method employed here. The results follow. As will be noticed, some of the samples were allowed to stand in ice over night to prevent any possible local heating, but the results do not vary much from those which were simply allowed to stand over night under ordinary conditions.

	First method. Decomposing im- mediately.	Second method. Standing for twelve hours before decomposing.	
		In ice.	Not in ice.
Same guncotton	198.1	202.8	202
	198.3	201.6	201.6
	198.0	202.3	202.6
		203.8	203.7
	201		208.2
			205.3
	201		204.3
			203
	202		205
			204
	200		205 (a)
	192.3		196.4
	200		194.7
	(a) In desiccator.		205.3

With a view of determining the cause of the above difference, a sample of guncotton weighing 0.6 gm. and analysed in the ordinary way (i.e., first method) read 119.7 c.c. on the nitrometer. The gas was run into strong commercial caustic potash solution and after saturation the loss of gas was found to be only 0.7 c.c.

Then into this caustic potash solution, saturated with nitric oxide, was run the gas obtained from one of the guncottons which had been analysed by the second method, and the result was as follows:—

First method..	..	..	..	200
Second method ..	..	..	..	205.3
After absorption ..	..	..	..	196.9

Several checks were made on the above with similar results.

We know that it is impossible for most of the results obtained by the second method to be correct, for extended researches have shown that guncotton having a nitration of 204 c.c. and upwards is not soluble in a mixture of two parts ether and one part alcohol, and yet all these guncottons tested were practically entirely soluble.

Effect of other Organic Substances.—The following experiments show the effect of the presence of various organic bodies and other substances (many of which occur in dynamites and gelatins) on the determination of nitrogen by the nitrometer.

In every case a weighed portion of potassium nitrate (about 0.55 gm) was taken and from 0.05 to 0.1 gm. of

substance was added. The mixture was allowed to stand over night in sulphuric acid and was then run through the nitrometer. Of course, in this case standing over night does not affect the result, as there is no organic matter present which can be decomposed, and the small amount of nitric oxide gas lost is constant in all determinations, including those in which the factors were determined.

Results are tabulated as follows:—

No.	Substance.	Amount taken. Gm.	Result in c.c.	Result with chromic acid.	Result after absorption with KOH.
1.	Resin	0.1	212.4		
2.	"	0.1		219.1	214.9
3.	Camphor	0.1	203.4		
4.	"	0.1		219.4	199.8
5.	Sulphur	0.1	225.3		
6.	"	0.15	227.3		
7.	Paraffin	0.1	199.5		
8.	"	0.05	209.5		
9.	Vaseline	0.2	217.6		
10.	"	0.05	218.7		
11.	MgCO ₃	0.05	223.4		
12.			221.0		

The following can be deduced from the results. All the organic compounds, as in 1, 3, 7, and 9, affect the results in such a way as to give low values. Paraffin has the greatest effect, then camphor, then resin, then vaseline. The effect of adding chromic acid, as seen by the absorption results of potassium hydroxide, is to oxidise some of the carbon to carbon dioxide and thus raise the results, but practically no more nitric oxide is obtained by this treatment. In the table, 2 and 4 show this.

The two inorganic substances used, sulphur and magnesium carbonate, on the contrary, tend to make the result a little high. This is explained in the first case by the formation of a little sulphur dioxide and in the second case by the formation of a little carbon dioxide, which is retained by the sulphuric acid and expelled during the violent shaking in the decomposing bulb. This latter is similar to the cases already cited where carbon dioxide is formed when organic nitrogenous compounds are allowed to remain over night in the sulphuric acid before decomposing in the nitrometer.

In summing up the above results we can at once see that the nitrometer is a very delicate instrument, by which, when all standard conditions are adhered to, very accurate results may be quickly obtained.

The scope of its usefulness, however, is somewhat limited, and a great number of details, apparently trivial, affect the results to a considerable extent.—*Journal of the American Chemical Society*, xxviii., No. 7.

THE DETERMINATION OF SILICA IN IRON ORES CONTAINING ALUMINA.

By GRAHAM DEAN.

I HAVE found that if the insoluble residue left on the treatment of an iron ore with acids is ignited for a short time the aluminium which it contains is converted into a form which dissolves in concentrated hydrochloric acid. On the basis of this fact the following rapid method for the determination of silica in such ores has been developed.

One gm. of the finely powdered ore is dissolved on the hot plate in concentrated hydrochloric acid, using an initial amount of 25 c.c. Boil until the iron is completely dissolved, adding two or three drops of nitric acid near the end. If pyrites is present, more nitric acid may be required. Nearly all iron ores will yield to this treatment; if an ore does not, the results are worthless.

Evaporate the solution to dryness, take up the residue with a small amount of concentrated hydrochloric acid, boiling till the ferric chloride is all dissolved. Dilute slightly, filter and wash thoroughly with hot hydrochloric

acid (1:1). If a determination of alumina is required, this filtrate must be examined as well as the solution obtained below.

Transfer the moist filter and residue to a platinum crucible and burn the filter carefully, as usual. Then set the crucible upright, put on the cover, and ignite for two or three minutes over a Dangler burner. I have found that the proper temperature is best secured in a dull or carbon covered platinum crucible. The ignition must not be continued too long and the temperature must be properly regulated.* I have repeatedly attempted to obtain good figures by use of bright and shining platinum crucibles, but have never been able to do so.

When cold the contents of the crucible are transferred to a beaker, the cake pulverised with a glass rod and digested for seven or eight minutes with boiling concentrated hydrochloric acid.† The residue should feel soft and mushy under pressure unless the silica of the ore existed as free sand. Dilute slightly, filter and wash thoroughly. The filtrate may be combined with the first filtrate for the determination of aluminium. The residue, after ignition, may be considered as practically pure silica.

The precipitation of the alumina by phenylhydrazine I have found most satisfactory. (Campbell and Hesse, *Journ. Am. Chem. Soc.*, xxi., 776; E. T. Allen, *Ibid.*, xxv., 423).

The figures given below are an average set selected from a large number of experimental determinations made with Mesabi ores containing in some instances a high percentage of alumina, a large portion of which was proved to be retained in the residue previous to separation and extraction. The results under the heading "Ignition" were obtained by the method given above.

	Ignition.	Sodium carbonate fusion.	Hydrofluoric acid.
1	12.86	12.83	12.94
2	22.06	22.82	22.99
3	17.50	17.40	17.56
4	5.16	5.00	5.10
5	6.05	6.00	5.99
6	13.89	13.80	13.70
7	9.84	9.92	10.06

The following amounts of alumina were found in residues obtained by the new method: 0.06, 0.04, 0.10, 0.11, 0.02, 0.07, 0.05, 0.09, and 0.10 per cent. Before the separation by ignition and treatment with hydrochloric acid the residues retained from 4.25 to 10 per cent of alumina. It is evident that the separation is sufficiently complete for technical purposes.—*Journal of the American Chemical Society*, xxviii., No. 7.

SOME EXPERIMENTS ON THE DETERMINATION OF VOLATILE COMBUSTIBLE MATTER IN COALS AND LIGNITES.‡

By E. E. SOMMERMEIER.

The method in general use in this country for the determination of volatile combustible matter is that recommended by the Committee on Coal Analysis appointed by

* Dr. Hillebrand explains the results obtained by Mr. Dean by calling attention to the fact that the aluminium of kaolin is rendered soluble hydrochloric acid by gentle ignition. (See McNeil, *Journ. Am. Chem. Soc.*, xxviii., 592). If the ignition is too intense, the aluminium becomes insoluble again. If this explanation is correct, the method would not be reliable for ores containing other silicates than kaolin.—*EDITOR JOURN. AM. CHEM. SOC.*

† One-fourth gm. of potassium chlorate added at this stage will give slightly higher alumina results, which are also more concordant with fusion alumina. No time is lost, since the seven or eight minutes allotted will suffice to remove chlorine from the solution as well as alumina from residue.

‡ Published by permission of the Director of the United States Geological Survey. Read before the Columbus Section of the American Chemical Society, May 23, 1906. From the *Journal of the American Chemical Society*, xxviii., No. 8.

the American Chemical Society (*Journ. Am. Chem. Soc.*, xxi., 1122—1126). The directions given are as follows:—

"Place 1 gm. of fresh, undried, powdered coal in a platinum crucible, weighing 20 or 30 grms. and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 c.m. above the top of the burner. The flame should be fully 20 c.m. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon. To find 'volatile combustible matter' subtract the per cent of moisture from the loss found here."

This is the method used in the volatile determinations made in the Chemical Laboratory of the United States Geological Survey Fuel Testing Plant, the only modification being that the flame is protected from air currents by enclosing in a cylindrical asbestos shield 15 c.m. long and 7 c.m. in diameter, the platinum triangle being located 3 c.m. below the top of the shield. The use of the shield gives more uniformity in the heat treatment with a corresponding greater uniformity of results. It is well recognised that variations in the size of the crucible, tightness of the lid, strength of the flame, &c., affect the process noticeably. Under uniform conditions the same operator usually has no great trouble with duplicates, but it is quite probable that different operators working even under only slightly different conditions would have considerable trouble in duplicating results.

In most coals the routine results obtained in the laboratory have checked to within less than 0.3 or 0.4 per cent; occasionally a sample has given trouble, and the variation between duplicates without any apparent reason was as great as 1 per cent. On some lignites it has been found impossible to obtain close duplicates, and on a few samples the carrying out of the official method gives very inaccurate results. This may be shown by the results obtained in the laboratory upon two different samples of the same lignite, which samples differed from one another only in the amount of moisture remaining in the air-dried sample, and perhaps in the fineness of the grinding. The results on Sample No. 1 are as follows:—

Moisture	9.88
Volatile matter	36.17
Fixed carbon	43.65
Ash	10.30
Sulphur	1.30

Sample No. 2.

Moisture	20.24
Volatile matter	58.48
Fixed carbon	10.85
Ash	10.43
Sulphur	1.03

This great difference in the fixed carbon results could not be accidental, as all of the results on both samples were duplicated. A series of determinations was begun to determine, if possible, the cause of this great variation. Two causes were suspected, and both were found to be partly responsible for the difference:—1. Mechanical loss due to the throwing out of solid particles by the too rapid expulsion of the volatile matter. The possibility of loss from this source is mentioned in the report of the Committee, but the results of their experiments are negative. 2. A different breaking down of the hydrocarbon compounds when expelled under different conditions and in the presence of variable amounts of moisture.

The results of Mr. N. M. Austin as published in the Committee's report showed that a preliminary treatment of the sample at a low heat and then the application of the full flame of the Bunsen burner gives higher results in fixed carbon than where the full flame of the Bunsen burner is applied from the beginning.

The proximate analysis of the sample of lignite giving

the unusual results was finally reported by the laboratory as follows:—

Moisture	20.24
Volatile matter	35.42
Fixed carbon	33.91
Ash	10.43
Sulphur	1.03

A series of seven results by the official method gave for volatile matter on this sample an average of 62.5 per cent with a variation between high and low results of over 12 per cent. Three results of volatile matter on this sample made after previous expulsion of the moisture at 105° gave average volatile matter 39.6 per cent with a variation between high and low results of 5.9 per cent. Preliminary treatment by driving off the moisture and most of the volatile matter at a low heat was then tried, the flame of the Bunsen burner being turned down to 10 c.m., and the crucible gradually heated. The application of the heat was regulated by holding the burner in the hand, and heating in such a way as to expel the moisture slowly, and gradually smoke off most of the volatile matter, the volatile matter escaping freely enough during the last minute of this preliminary heating to burn with a small flame around the edge of the crucible cover. Two results with five minutes of preliminary heating and then seven minutes over the full flame of the Bunsen burner gave an average in volatile matter of 35.08 per cent, the variation between the two results being 0.23 per cent. Two results with three minutes' preliminary heating and seven minutes over the full flame of the Bunsen burner gave an average of 35.6 per cent with a variation of 0.75 per cent between results. A result obtained by four minutes of preliminary heating and then seven minutes over the full flame gave 35.42 per cent. The difference in the results obtained by the three, four, and five minute preliminary treatment is small, and in all subsequent experimental tests the time of the preliminary heating was four minutes. To determine the mechanical losses and difference in volatile compounds given off, a number of ash determinations were made after the driving off of the volatile matter by the official method, and after driving off the volatile matter in connection with the preliminary heating. The results of volatile matter and ash on three determinations by the official method are as follows:—

Volatile matter	66.72	67.47	54.82
Ash	4.30	4.38	7.25 (a)

(a) This result is possibly explained by the fact that this sample stood for two hours in the crucible after weighing out, and a considerable amount of the moisture content may have escaped before the sample was treated for the determination of the volatile matter.

Two determinations with four minutes of preliminary heating and then seven minutes over the full flame gave:—

Volatile matter	36.06	36.65
Ash	11.16	11.15

That mechanical losses occurred during the rapid evolution of the volatile matter by the official method was also indicated by the shower of solid carbon particles driven off as sparks during the first few minutes, while with the preliminary heating these sparks were nearly or entirely absent. The average volatile matter on the first two determinations was 67.1 per cent, the average ash 4.34 per cent. The average volatile matter on the two results by the modified method was 36.35 per cent, ash 11.15 per cent. The moisture in the sample determined at this time was 19.78, giving fixed carbon 32.72 per cent. The difference in the ash results on the two pairs is 6.81 per cent, or the amount of sample driven off mechanically by the regular method is $6.81 \div 11.15$, or 61 per cent. Taking this portion of the fixed carbon result by the modified method gives 20 per cent as the amount of fixed carbon expelled mechanically in the first determinations.

The results on the official process after making this correction and also taking the correct ash value are as follows:—

Moisture	19.78
Volatile matter	47.10
Fixed carbon	41.97
Ash	11.15
100.00	

After making this correction for mechanical losses the difference in the fixed carbon by the two processes is still 10.75 per cent, which difference must be due to the difference in the breaking down of the hydrocarbon compounds by the different heat treatment. The ash from the third result by the official method was 7.25 per cent, or the loss of ash 3.9 per cent. Correction for fixed carbon mechanically carried off is accordingly 3.9/11.15 or 11.4 per cent. The result, after making the fixed carbon and ash corrections, figures as follows:—

Moisture	19.78
Volatile matter	43.42
Fixed carbon	45.65
Ash	11.15
100.00	

The difference in this case in fixed carbon by the two methods due to the different heat treatment is 7.07 per cent.

Effect of Fineness of Sample.—This particular sample was very finely ground. To find out how much this difference in result was due to the fineness of grinding, a duplicate portion of the same sample was ground down till it passed a 40-mesh sieve. The results of duplicates by the official method and the modified method obtained are as follows:—

	Official method.	Preliminary heating.
Volatile matter ..	42.07	35.72
Ash	10.25	11.20

Or loss in ash 0.95 per cent. The proximate analysis of the sample by the modified method is as follows:—

Moisture	19.35
Volatile matter	35.72
Fixed carbon	33.73
Ash	11.20
100.000	

The correction for fixed carbon to be applied to the result of the official method is 0.95/11.20 or 8.5 per cent of the fixed carbon result of the modified method, which is 2.9 per cent. The results by the official method after correcting for mechanical loss of fixed carbon and ash are as follows:—

Moisture	19.35
Volatile matter	39.17
Fixed carbon	30.28
Ash	11.20
100.00	

The difference in fixed carbon between the two methods due to different heat treatment is 3.45 per cent. These results show, at least for lignites, that the fineness of the sample has an important effect upon the result. Upon another sample of lignite similar to the one already tested, except that it contained more moisture (30.45 per cent), the results obtained are as follows:—

Average of results by the modified process—

Moisture	30.45
Volatile matter	30.97
Fixed carbon	27.75
Ash	10.83
100.00	

The results in volatile matter and ash by the official method—

Volatile matter	44.40
Ash	8.12

Hence, the correction to be applied to the fixed carbon and ash for mechanical loss is 2.71/10.83. Applying these corrections, the results by the official method are—

Moisture	30.45
Volatile matter	37.43
Fixed carbon	21.29
Ash	10.83
100.00	

The difference in the fixed carbon results between the two samples due to different heat treatment is 6.46 per cent.

To test the effect of the fineness of grinding upon the determination of the volatile matter in ordinary bituminous coal, a sample of Kentucky coal containing 2 per cent moisture, 5.7 per cent ash, and 0.9 per cent sulphur was still further reduced in ash content by floating on a calcium chloride solution, sp. gr. 1.32. The lighter portion was then thoroughly air-dried and separated by sifting into the following sizes:—One-fourth to one-tenth, one-tenth to one-twentieth, one-twentieth to one-fortieth, one-fortieth to one-eightieth, and one-eightieth and finer. The proximate analyses of the samples by the official method are as follows:—

	Moisture.	Volatile matter.	Fixed carbon.	Ash.
1/4 to 1/10 ..	1.15	39.05	58.20	1.60
1/10 to 1/20 ..	1.45	38.80	58.55	1.20
1/20 to 1/40 ..	1.70	38.55	58.35	1.40
1/40 to 1/80 ..	1.90	38.05	58.40	1.65
1/80 and finer ..	2.05	35.54	59.66	2.75

By the modified process with four minutes of preliminary heating the result in volatile matter on the one-twentieth to one-fortieth size was 33.75 per cent and on the one-eightieth and finer 32.85 per cent.

The results in volatile matter on these different sizes are somewhat higher on the coarse samples. However, the different ash contents of the different sizes indicate that the sizing had to a degree separated the coal into somewhat different varieties, as the higher ash content of the finer sample would not in itself be sufficient to account for the lower volatile results. In order to see whether the difference was due to the fineness of grinding or difference in the coals, a portion of the one-twentieth to one-fortieth sample was ground down in an agate mortar and the volatile matter determined on this fine portion. The average of several results was 37.6 per cent as against 38.55 per cent on the coarse sample.

From this series of results it appears, at least in low moisture bituminous coals, that the finer ground samples give somewhat lower volatile matter than the coarser samples, probably due to the more complete sintering together of the fine samples upon heating, with the consequent effect upon the giving off of the volatile matter.

Effect of Different Heat Treatment.—In order to find out how much effect different heat treatment has on different coals, a series of samples was selected ranging from anthracite to peat, most of the samples used in the tests having been previously more or less completely air-dried so as to permit of better handling in the laboratory. Determinations for volatile matter were made in duplicate by the regular official method and by the four-minute preliminary heating method. The proximate analysis of the samples with the volatile matter determined by the official method is tabulated in the first five columns; the results for volatile matter by the preliminary heating are given in the sixth column; the differences in volatile matter by the two methods are given in the seventh column. The determinations for moisture were all made in accordance with the official method by weighing out a separate sample.

The same is true of the determinations for ash with the exception that upon two or three of the lignite samples and one of the Pennsylvania samples the results for ash are those obtained after the determination of the volatile matter by the modified process. These particular samples and results are all specifically mentioned elsewhere in this paper.

Source of coal.	Moisture.	Official method. Volatile matter.	Fixed carbon.	Ash.	Sulphur.	Volatile matter with four mins. preliminary heating.	Difference.
Colorado anthracite ..	2.80	5.05	77.55	14.60	0.60	1.90	0.15
Arkansas ..	0.83	12.47	72.05	14.65	2.14	12.37	0.10
Pennsylvania ..	0.90	17.35	74.92	6.83	0.97	16.07	1.28
Pennsylvania ..	1.05	33.10	53.30	12.55	1.76	30.35	2.75
Kentucky ..	2.99	37.51	56.68	2.82	0.58	34.78	2.73
Indiana ..	4.20	37.70	45.65	12.45	4.13	34.67	3.03
Washington ..	6.65	35.87	44.57	12.91	0.68	34.23	1.62
Indiana ..	8.40	34.40	48.72	8.48	1.47	32.00	2.40
North Dakota (lignite) ..	11.65	45.58	32.97	9.80	1.04	40.17	5.41
Illinois ..	12.40	32.18	42.82	12.60	1.30	30.12	2.06
Texas lignite (fine) ..	19.78	62.50	6.57	11.15	1.03	35.42a	27.08.
Texas lignite (40-mesh duplicate) ..	19.35	42.07	27.38	11.20	—	35.72	6.35
Texas lignite not air-dried	30.45	44.40	15.42	9.73	—	30.97	13.43
Massachusetts peat ..	13.25	49.80	16.21	20.74	0.58	47.92	1.88

a. Two determinations upon the fine sample of Texas lignite made by heating for four minutes over a flame 5 c.m. high and then seven minutes over the full flame (25 c.m.) gave 35.47 per cent volatile matter. Almost an exact check upon the result obtained by the four-minute preliminary heating with a 10 c.m. flame regulated by holding burner in the hand.

With the exception of the anthracite and semi-anthracite samples, the results by the preliminary heating as compared with the official method all show a considerably less amount of volatile matter and a correspondingly greater amount of fixed carbon. In the case of the lignites, the greater volatile matter by the official method, as has been shown, is partly due to mechanical losses.

In order to see if mechanical losses might account for the differences on the bituminous coals, determinations for the ash after the determination of the volatile matter were made on one of the Pennsylvania samples. The average results for ash on the sample by the two methods are as follows:—

Official method	Ash.
Preliminary heating	12.56
	12.53

These results indicate no mechanical loss whatever, and in none of the samples except the lignites were visible solid carbon particles driven off in the form of sparks, and the differences must be ascribed to the different breaking down of the hydrocarbon compounds by the difference in heat treatment.

Effect of the Presence of Moisture.—Comparisons of the results of volatile matter on a great number of samples differing from one another in moisture content indicate that the presence of loosely held moisture in the sample causes a higher volatile result. In order to obtain more definite data on this question three samples low in moisture and representing widely different kinds of coal were selected for a series of determinations. The effect of loosely held moisture upon the determinations for volatile matter in each of these samples was determined by adding

to the sample after weighing out definite amounts of water, which was thoroughly mixed with the sample by means of a fine platinum-wire, and the volatile determination then made in the usual manner according to the official method. The first sample selected was a sample of Pennsylvania coal. The proximate analysis of the air-dried sample is as follows:—

Moisture	1.05
Volatile matter	33.00
Fixed carbon	53.30
Ash	12.55
Sulphur	1.75

The results for volatile matter in this sample determined in the presence of additional moisture are as follows:—

	Volatile matter.
With 0.05 grm. additional moisture ..	33.6c
" 0.1 " " " " "	33.70
" 0.15 " " " " " "	33.80
" 0.2 " " " " " "	34.10
" 0.3 " " " " " "	33.90

The second sample was an air-dried sample of Illinois coal, the proximate analysis of which by the regular official method is as follows:—

Moisture	1.35
Volatile matter	39.35
Fixed carbon	44.65
Ash	13.65

The results of volatile matter with the additional moisture added to the sample are as follows:—

	Volatile matter.
With 0.03 grm. additional moisture ..	39.60
" 0.05 " " " " " "	39.30
" 0.10 " " " " " "	40.00
" 0.15 " " " " " "	40.05
" 0.2 " " " " " "	39.75

The third sample was an air-dried sample of Arkansas lignite, the proximate analysis of which by the official method is as follows:—

Moisture	10.85
Volatile matter	38.50
Fixed carbon	31.40
Ash	19.25
Sulphur	0.83

The results for volatile matter with the additional moisture are as follows:—

	Volatile matter.
With 0.05 grm. additional moisture ..	40.35
" 0.10 " " " " " "	41.20
" 0.15 " " " " " "	40.90
" 0.20 " " " " " "	44.90

Without exception all of these results show that the presence of loosely held moisture in the sample increases the value obtained for the volatile combustible matter. The average increase for the Pennsylvania sample is about 0.7 per cent. On the Illinois sample the increase for volatile matter is 0.4 per cent. On the Arkansas lignite the increase is 3.3 per cent.

To see what effect this loosely held moisture might have on the volatile determinations where the sample was first subjected to four minutes of preliminary heating over a low flame, determinations were made upon these samples with and without additional moisture. The results are as follows:—

Pennsylvania sample with no moisture added, volatile matter 30.35. With 0.3 grm. added, the volatile matter 31.65.

The Illinois sample with no moisture added, volatile matter 34.85. With 0.15 grm. moisture added, volatile matter 36.10.

The lignite sample with no moisture added, volatile matter 36.90. With 0.2 grm. moisture added, 37.40.

These results show that even with a gradual preliminary heating the presence of loosely held moisture increases the value of the volatile determinations, the difference in some of the samples being as great as the difference by the official method, from which it appears that the rapid application of heat sufficient to drive off this moisture results in a reaction between the water vapour and the carbon or hydrocarbons in the coal.

Conclusions.—The results of the foregoing experiments and tests show that the value obtained for volatile matter in coal is affected to an important degree by the method of heating the sample, by the fineness of pulverisation, and by the amount of loosely held moisture present. In bituminous coals these differences do not exceed 3 or 4 per cent, and appear to be entirely due to a different breaking up of the hydrocarbon compounds under the different conditions of heat treatment, fineness of sample, and amount of moisture present. In the case of lignites where the difference may be as high as 25 per cent this difference is largely due to the mechanical loss in the sample during the rapid expulsion of the volatile matter.

Correctness of Results.—Since the determination of the volatile matter is a purely arbitrary one unless mechanical loss can be shown, as in the case of lignites, it appears that any results obtained by following out the regulation method should be considered as correct, any difference in results due to differences in fineness of pulverisation or to the amount of moisture present having no effect upon the correctness of the value actually obtained. The differences due to difference in pulverisation or moisture content do, however, have a very important effect when it comes to the question of different chemists obtaining concordant results upon different samples of the same coal.

In regard to the difference in results obtained due to a different heat treatment, while the method of heating as given by the official method may be considered as giving the correct result, it does not necessarily give us a result approximating very closely the volatile matter as given off when the coal is fired under a steam-boiler or especially when coked in a coke oven, as under these conditions the volatile matter is driven off gradually and during a considerable interval of time, and it appears that the slower driving off of the volatile matter from the sample in the laboratory gives results more in accordance with these conditions than does the official method. This latter fact is, however, a matter of minor importance, for so long as all volatile determinations are done in the same way it makes very little difference what that way is.

In the case of lignites where the application of the official method causes mechanical losses it appears desirable and necessary that the Committee so modify the official method for volatile matter in lignites as to prevent this loss, and the results of these foregoing determinations and experiments are published at this time with a view of bringing this matter before the Committee and the public.

DISCOLORATION OF FRUITS AND VEGETABLES PUT UP IN TIN.

By F. A. NORTON.

A NUMBER of cases of discoloration of fruits and vegetables put up in tin have come to the attention of the writer. In most cases the discoloration was undoubtedly due to sulphides of the heavy metals, the discoloration in some cases being confined to the container, in others affecting the fruits and vegetables as well. The source of the hydrogen sulphide varied in different cases. Some micro-organisms are capable of evolving hydrogen sulphide through breaking down of proteid matter, but this would result only with goods which were not properly sterilised and is not so frequent as some other causes. Also such goods are unfit for

consumption, so that the discoloration is of minor importance. In other cases hydrogen sulphide resulted from the use of sulphites in connection with fruits, reaction having taken place between the sulphites and vegetable acids with the liberation of sulphurous acid, which, acting upon the tin of the container, had produced hydrogen sulphide. Another source of hydrogen sulphide was the decomposition of proteid matter through the use of an exceptionally heavy process by the action of steam under pressure on the proteids. Where discoloration had taken place in the goods, the source of the heavy metals was the tin plate and solder of the container.

All fruits and vegetables, as has been shown by Leach ("Food Inspection and Analysis," p. 696), have a greater or less solvent action upon the tin plate and solder of the container, taking up variable amounts of tin and lead, the extremely acid fruits, like rhubarb, being most active, though some of the vegetables, such as squash and pumpkin, take up very large amounts of tin.

Having pointed out the source of the heavy metals and the hydrogen sulphide, one can very readily understand how the discoloration of these goods would take place. A history of some cases in point will best illustrate the different forms of discoloration.

Recently, some badly discolored pears were sent in to the laboratory for examination. On opening the can a heavy brownish black deposit was discovered over the inside of the can, and wherever the pears came in contact with the can there was also the same deposit on the fruit, rendering it unsightly and unfit for the market. Previous experience by the director of the laboratory, Mr. E. W. Duckwall, at once suggested that sulphites had been used in the preparation of the fruit, and that the discoloration was probably due to their use. Determinations for sulphites were made and they were found to be present in very large quantity. The character of the discoloration, which almost assumed the form of a deposit, suggested to us that it was due to metallic sulphides, principally tin sulphide, resulting from the reaction between the sodium sulphite, vegetable acids, and tin.

In order to ascertain whether this was the case or not, pieces of pear of good colour were placed in two beakers with pieces of tin and solder in each. To one sodium sulphite was then added and the other simply left in water. The pear not treated with sodium sulphite kept its colour perfectly on standing in contact with the tin and solder, but the pear in the beaker to which sulphites had been added soon began to darken, and in the course of two or three days the same brownish-black appearance observed in the discoloration of the pears in the case at hand had permeated nearly the whole pear tissue of the sample under treatment in the beaker. Some of the brownish deposit, also some of the discolored fruit from the can showing the discoloration, was treated with strong hydrochloric acid, which immediately destroyed the discoloration of the pear tissue and brought the deposit into solution. On diluting, filtering, and precipitating with hydrogen sulphide, a small quantity of tin sulphide was obtained, which indicated that the discoloration was due to sulphide of tin and other metallic sulphides. This was further confirmed by treating the inside of the discolored can in which the pears had been put up with strong hydrochloric acid, and testing the fumes given off with lead acetate paper for hydrogen sulphide. A very positive reaction was obtained for sulphides, which was confirmed by other tests. In fact, the odour of hydrogen sulphide evolved from the decomposition of the sulphides seemed to be unmistakably present. This experimental data seemed to show conclusively to us that the discoloration was due to metallic sulphides resulting from the hydrogen sulphide which had been liberated by reaction between the sulphites and the tin, aided by the fruit acids present.

To further test this view pieces of tin-foil were treated with sodium sulphite and also with sulphurous acid solution. The tin-foil in the sulphurous acid solution quickly became discolored with a considerable brown deposit,

which was shown to be tin sulphide, while that in the sulphite solution remained perfectly bright. This would indicate that there would not be much danger of discoloration from reaction between sulphites and tin in a neutral medium, but that where sulphurous acid would be liberated discoloration would be very sure to result.

Other pieces of tin-foil were then treated in beakers with sodium sulphite solution to which various acids, such as acetic, lactic, tartaric, citric, and others, had been added. In each case discoloration resulted, showing that the vegetable acids had liberated sulphurous acid, which in turn reacted with the tin to form tin sulphide, giving the discoloration. Most fruits contain appreciable amounts of such acids as citric and malic acid. In some cases, where fermentation has taken place to any extent, acetic or lactic acid is present, and fruits or vegetables containing any of these organic acids, if treated with sulphites, are very sure to produce discoloration.

Soldering fluxes sometimes are somewhat acid, and if a little excess is used, permitting the acid to come in contact with the goods, if these are treated with sulphites, discoloration is very sure to be observed at points where the acid has come in contact with the fruit or vegetable. While it would seem that sulphites can be used without any danger of discoloration in neutral substances, there certainly is much danger of discoloration if they are used in products of a somewhat acid character put up in metal containers.

Discoloration from hydrogen sulphide evolved through the employment of a heavy process is illustrated by the following case:—In order to secure the proper cooking of the large siftings of peas, which was not readily accomplished in the blancher, the packer had lengthened the process to fifty-five minutes at 240°, with the result that this pack of peas contained a very large percentage of cans containing discolored peas, while the smaller siftings of peas given a shorter process were free from the discoloration. An examination of the peas in the containers showed the cans to be very much discolored, the inside of the can being of a brownish purple colour, though there was nothing in the shape of a deposit. The discoloration of the peas was confined more particularly to those around the outer portion of the can, and the discoloration did not extend into the peas to any great extent. Some of the more badly discolored peas were separated out and a determination of tin made, which was found to be present in considerable quantity. Also the discoloration, both of the peas and the can, was soluble in strong hydrochloric acid, which would be the case with tin sulphide. Reactions for hydrogen sulphide were obtained from the inside of the can quite readily, both with lead acetate paper and sodium nitroprussiate. This same discoloration of the can is noticeable wherever a heavy process is employed and had previously been found by the writer to react for sulphides, evidently being due to tin sulphide formed through hydrogen sulphide liberated during the processing. There is seldom discoloration of the contents, but in this case it seemed that sufficient hydrogen sulphide had been liberated, together with the tin and lead taken up by the contents of the can, to produce the discoloration. Experiments which have been made show that when proteid substances are acted upon by steam under pressure ammonia and hydrogen sulphide are split off from the proteid molecule, with the formation of albumose and peptone. Dr. Long, in his recent work, in his discussion of proteid substances ("Physiological Chemistry," p. 74), gives special attention to the decomposition of proteid substances, by steam under pressure, stating that if the temperature is high enough the reaction will extend even beyond the formation of ammonia and hydrogen sulphide, resulting in the complete destruction of the proteid molecule. This would explain the source of the hydrogen sulphide, and, taking into consideration the fact that tin and some lead would have been taken up by the peas, would explain the discoloration of the goods.

In order to assure ourselves that sufficient hydrogen sul-

phide would be produced under a very heavy process to cause the discoloration, two glass jars were filled with peas and to one 50 m.grms. of stannous chloride were added, and both were processed at 240° for an hour. The peas in the jar to which the tin chloride had been added showed a very marked brown discoloration, from which the other peas were entirely free, which would confirm our findings in this case.

In some cases, especially in corn, we have encountered a discoloration which was more local in character than in the case of the peas just described. In this case the discoloration was confined almost entirely to the vicinity of the seams and cap. As corn is a very stable product and does not change its position in the can, it would appear that the discoloration in this case had come more particularly from the solder or from an excess of flux. It has been shown that where a poor grade of solder containing a large amount of lead is used, the action of the fruit or vegetable juice is greater, more metal being brought into solution. Also if an excess of soldering flux, especially if somewhat acid in character, should remain along the seam, it would result in more of the metal of the container being taken up by the contents of the can at those points, and then on liberation of hydrogen sulphide during the process discoloration would result at those points, while the contents of the can otherwise would be free from discoloration.

From the above, it can be stated that sulphites should not be used with goods of an acid character which are to be put up in tin. Where a heavy process is necessary, care should be exercised to avoid the use of an excess of flux or the use of low-grade solder or tin-plate which would tend to increase the amount of heavy metals taken up by the goods. Also the length of the process, in order to avoid evolution of hydrogen sulphide, should be as short as possible, consistent with complete sterilisation of the goods. —*Journal of the American Chemical Society*, xxviii, No. 10.

PROCEEDINGS OF SOCIETIES.

FARADAY SOCIETY.

Ordinary Meeting, December 11th, 1906.

Dr. T. M. LOWRY in the Chair.

DR. A. C. C. CUMMING read a paper entitled "*Contributions to the Study of Strong Electrolytes.*"

I. *The Elimination of Potential due to Liquid Contact.*—Certain solutions have the property of reducing the potential due to the contact of two solutions, and potassium chloride has been used for this purpose. In most cases a saturated solution of potassium chloride does not remove all the diffusion potential; indeed, if the solutions in the cells be strong, it only removes a small part. This property of removing more or less of the diffusion potential depends on two factors in the connecting solution: firstly, the positive and negative ions must be of equal velocity; and, secondly, the concentration of the connecting solution must be high compared with the solutions in the cells.

The author suggests a saturated ammonium nitrate solution as that which fulfils these two conditions better than anything else at present known, and shows by experiments with different cells that this is the case.

A curious point was noticed when two cells containing the same solution, but of different concentrations, were joined by a third solution of the same substance. Whatever the strength of this third solution, the observed potential remained the same as when the two cells were directly connected with one another. This has not been recorded before, but could have been predicted from Nernst's theory.

II. *The Potentials of Silver Nitrate Solutions.*—The electromotive force between silver nitrate solutions of

various strengths from N/1000 up to N/2 was measured as accurately as possible. Three kinds of silver electrodes were used, and various methods were tried to eliminate the small amount of diffusion potential.

The results proved that for silver nitrate the electromotive force gives the same measure of the ionic concentrations as is obtained from the conductivities, and therefore support the view that the conductivity gives a true measure of the ionic concentration.

Mr. N. T. M. WILSMORE said that the author's method of eliminating liquid contact potential was a distinct advance on Planck's formula which was limited in its application.

A paper on "*The Electrochemistry of Lead*" was then read in abstract by Dr. A. C. C. CUMMING.

The tendency of any ion (*i*) to be transformed into an ion (*o*) with a lower valence may be measured by means of an oxidation electrode. If *n* be the difference in valence of the two forms, the E.M.F. in volts—

$$= P + \frac{0.0591}{n} \log_{10} \frac{C_i}{C_o} \text{ (at 25)},$$

where the symbols have their usual meanings.

A solution containing plumbic lead was obtained by dissolving PbO₂ in nitric acid, and the amount estimated analytically, while any desired strength of plumbous lead was obtained by addition of ordinary lead nitrate. The potentials were measured with a lead peroxide electrode, against a N calomel electrode, with a saturated ammonium nitrate solution as connection. The mean value for P, *i.e.*, the tendency Pb⁺⁺⁺ → Pb⁺⁺, was found to be +1.82 volt against the hydrogen standard electrode. The value for Pb⁺⁺ → Pb was also re-determined, and found to be -0.137 volt, so that the value for Pb⁺⁺⁺ → Pb is +0.84 volt.

Some experiments were carried out to find how the addition of nitric acid affected the ionisation of lead (plumbous) nitrate. The solubility of lead nitrate was shown to decrease very rapidly with increase of the nitric acid concentration.

Measurement of the plumbous ion concentration in alkaline nitrates showed that this varied greatly in different solutions, and the results proved that there was considerable complex formation between KNO₃ and Pb(NO₃)₂, but not so between NaNO₃ and Pb(NO₃)₂.

The results in general prove that lead in the tetrad form is a highly electro-positive element, and also direct attention to a curious difference in the behaviour of sodium and potassium nitrates towards lead nitrate.

Mr. N. T. M. WILSMORE remarked on the bearing of the author's experiments on the theory of accumulators as propounded by Dolezalek. A theory based on tetravalent ions would be more satisfactory than that built up by Dolezalek on the theory of PbO₂ ions assumed by Liebenow.

A paper by Mr. R. W. VICAREY on "*Storage Batteries and their Electrolytes*" was, in the absence of the author, read in abstract by the Secretary.

The paper is a continuation of one read by the author in July, 1905, and deals chiefly with some of the problems involved in the manufacture of accumulators, particularly as regards the effect of nitrogen and other impurities introduced consciously or by accident in the process of manufacture. Nitrogen compounds are often used, and advisedly so in the opinion of the author, for assisting in the oxidation of the positive plates, and in such cases it is essential that every trace of nitrogen be removed before the cells leave the works, in spite of the difficulties, which are insisted upon, involved in its complete elimination. The evils attributed to nitrogen, both after complete formation and in the latter stages of the forming processes, are described in detail. Among other troubles, the author has observed the formation of an irreducible and unoxidisable sulphate of lead, 2PbSO₄.PbO, a detailed study of the effects of which are promised for a future communication.

The evil effects of nitrogen are greatly accentuated by the presence of other impurities—notably iron, an element likewise very difficult to eliminate—and experiments are described illustrating these effects, which become more serious with decreasing current densities. Researches of Peters, Elbs, and Bell are quoted in support of the author's main contentions.

Mr. H. L. JOLY criticised in detail many of the author's contentions. He could not accept the extreme "ammonia" theory claimed by the author, who had not furnished sufficient definite and reliable data to found hypotheses upon. He would like to have had an account of the physical contents of the "new" lead sulphate. After hearing Dr. Cumming's paper, he was surprised that the author had used platinum, and not the more reliable lead electrodes in his experiments on the effect of impurities. The accentuation of separate effects of ammonia and iron by combining them together was of great interest, but the experiments needed elaborating.

CORRESPONDENCE.

MELTING-POINT OF CARBON.

To the Editor of the Chemical News.

SIR,—The following little calculation *re* the melting-point of carbon occurred to me, but it is so obvious, and also so indefinite, that I hesitate to send it to you.

From Van der Waals' equation we learn to compare substances relatively to their critical constants. According to Weber, the atomic heat of graphite seems to tend to a limiting value at high temperatures. Taking his last few numbers, somewhere about 2000° seems to be the point at which the mean 6.4 would obtain. Now oxygen solidifies at 50° absolute, and its critical temperature is 155.8° on the same scale; therefore the temperature at which solid oxygen would give the mean value for its atomic heat must have limits of 0—50° absolute. If we take the mean 25°, and apply the ratio of its critical temperature to this temperature to the case of carbon, we get approximately—

$$\frac{155}{25} \times (2000^\circ + 273^\circ), \text{ or about } 14,000^\circ \text{ Abs.,}$$

as the critical temperature of carbon.

Applying now the oxygen relationship again to this result we get $\frac{50}{155} \times 14,000^\circ \text{ Abs.}$, or somewhere about 4000° C., as the melting-point of carbon, which is interesting from the fact that Crookes places it, I believe, at about 4100° C.—I am, &c.,

R. H. McCRAE.

New College, Herne Bay,
December 8, 1906.

THE ORIGIN OF JET.

To the Editor of the Chemical News.

SIR,—As the translator into English of Neuburger and Noalhat's "*Technology of Petroleum*," in which the different theories as to the origin of petroleum are discussed at some length, and as a teacher of geology and mineralogy, I am interested in Mr. Spielmann's article on the origin of jet, which also incidentally touches on the origin of petroleum (CHEMICAL NEWS, xciv., p. 281). The question seems a difficult one, as the evidence which points one way seems to be refuted by equally strong evidence in an opposite direction. I am rather surprised that Mr. Spielmann should ignore the electrical properties of jet as affording a clue to its origin. "Jet," says Bishop Watson, "however, when warmed by friction has the power of attracting bits of straw, feathers, and other light bodies, but I have never observed this property in any of the cannel coals which I have tried" ("*Chemical Essays*," 1782, vol. iii., p. 11).

This electrical property and its association with the fossil remains of conifers points to jet having a common origin with amber. This theory of mine is further confirmed by Bishop Watson's account of the geological occurrence of amber and his theory of its formation, which in some points seems to tally with Mr. Spielmann's theory of the origin of jet. "The superincumbent strata are sand, fossil wood, pyrites; sand, again, in which the amber is found—sometimes in detached pieces, sometimes in little heaps. This distribution of the strata where amber is found, together with their proximity to the sea, has led it to be inferred with some probability that this mineral owed its situation to the inundation and reversion of the sea, and that it was derived partly from an oil arising from the decomposition of vegetables by subterranean fire, and partly from a mineral acid. Amber is frequently found in Italy, where they have no fossil wood but get plenty of petroleum" (*loc. cit.*, pp. 13, 14).

Is jet metamorphosed amber or resin? As to the intermediate jet products referred to by Mr. Spielmann, I should say the electrical capacity of the jet would be a better guide than the polish. Then there are the destructive distillation products to be considered. I do not recollect having seen a full statement of the latter.

Again, ground paraffin shale is a useful pigment (mineral black), but if massive jet be a brilliant black, powdered it is a dirty grey. Why? May I be allowed to protest against the introduction of radio-activity to explain the origin of jet, where it seems as unnecessary as it would be if introduced to explain the origin of rosin-pitch or bone-pitch (pitches which rival natural asphaltum in lustre, but very intractable as regards solvents). Volcanic gases would separate impure carbon from crude bone-tar. The fact may be of theoretical importance. "Radio-activity" seems to me through abuse of the term to be destined to exert as retarding and pernicious an influence on the progress of chemistry as the phlogiston of old.

On more than one occasion I have started this distillation and collected the petroleum-like fractions apart, but had eventually to discard them for lack of opportunity to work them up. I used up to equal weights of rosin and sulphur, and got in each case several different coloured distillates of different viscosities. Needless to say, a strong mercaptan-like odour was given off during the distillation, but I made no attempt to collect the gas.

Will some one else with better opportunities take up the subject? I am sure it would pay well for thorough threshing of it out.

Were it not that the difficulty would have to be encountered as to how petroleum is met with so far down in the geological scale, I would suggest that petroleum is a caoutchouc or gutta derivative. It only requires the shifting of the earth's axis to make our present caoutchouciferous and guttiferous zones coincide with the petroleum lines of strike of the present day. Rubber is the only vegetable product which yields gasolene on destructive distillation.

Trusting you will find room for these remarks on an interesting subject, they only seem the natural development of certain points in Mr. Spielmann's article, which is, in fact, a plea for the resiniferous origin of petroleum and jet. Interesting results as to origin of petroleum might be got from a chemical point of view by distilling rosin with sulphur.—I am, &c.,

JOHN GEDDES MCINTOSH.

9, Parsonage Street, Cubitt Town, E.

P.S.—On re-studying the article, the following sentence on p. 282 still further accentuates the force of my contention that jet is a resin derivative akin to the hard pitch from a rosin still:—"And in some specimens where partial fossilisation has occurred jet has formed that part of the wood unpreserved by the substituting materials." These are very evidently resiniferous vessels, resin pockets, &c., which for several and very evident reasons resisted the pseudomorphous transformation.—J. G. M.

HELIUM OR HELION?

To the Editor of the Chemical News.

SIR,—Is the termination *um* still regarded as characteristic of metallic elements and *ion* of non-metallic elements? If so, why is it not decided to write *helion* instead of *helium*; or is it that the metallic nature of the element has been placed beyond all doubt?—I am, &c.,

S. ARCHD. VASEY.

Bromley, Kent, December 19, 1906.

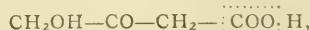
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 24, December 10, 1906.

A Colour Reaction of Reducing Sugars given by Alkaline *m*-Dinitrobenzene.—MM. Chavassier and Morel.—The authors have made numerous applications of the reaction of aldehydic and ketonic sugars upon *m*-dinitrobenzene in a strongly alkaline medium, which by their reducing action give rise to the formation of a violet colouring matter, turning yellow with mineral acids. The following results were obtained:—1. With saccharose, no coloration; with maltose and lactose, violet coloration after some minutes; with dextrose, galactose, and arabinose, violet coloration after some minutes; with levulose, violet coloration in less time; with glycogen, no coloration. The weaker the solutions of the sugars the longer the time taken to produce the violet coloration. 2. Other reducing substances besides the sugars give colorations with the same reagent, e.g., aldehydes and ketones without the alcoholic group give a red coloration, which would mask the violet coloration of the sugars; therefore, in employing *m*-dinitrobenzene for the sugars, it is necessary to be assured of the absence of aldehydes and ketones. Uric acid gives the same coloration as the sugars, and must be eliminated before research upon the sugars can be proceeded with. 3. Albumins, albumoses, acid amides, urea, creatine gave no reaction. Hence the violet coloration given with *m*-dinitrobenzene serves equally with the other usual methods for detecting the presence of the reducing sugars, and it has the advantage of great ease of execution.

A Tetrabrom-derivative of Methyleneethylketone.—M. Pastureau.—The author has obtained a new body, tetrabrom-methyleneethylketon, $C_4H_2OBr_4$, by the action of bromine upon the superoxide of methyleneethylketone prepared by the action of acidified hydrogen peroxide upon methyleneethylketone. Hitherto only monobrom-derivatives and a hexabrom-derivative of methyleneethylketone, $CH_3-CO-CH_2-CH_3$, have been known. The tetrabrom-derivative consists of white octahedral crystals, insoluble in water, soluble in boiling alcohol, little soluble in cold alcohol. The constitution, determined by saponification with an aqueous solution of potassium carbonate, appears to be $CH_2Br-CO-CH_2-CBr_3$, since an acid β -ketonic alcohol is produced,—



which readily decomposes, and gives acetol by losing CO_2 .

MEETINGS FOR THE WEEK.

TUESDAY, Jan. 1st.	} Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Signalling to a Distance, from Primitive Man to Radiotelegraph" (Experimentally Illustrated), by W. Duddell, M.Inst.E.E.
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